620.5
U58
B93j
anal O
SEP 10 1930

U. S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 5 AUGUST, 1930 No. 2

CONTENTS

RP. No.	TITLE AND AUTHOR	Page
194.	Fire clays. Some fundamental properties at several temperatures. R. A. Heindl and W. L. Pendergast	213
195.	A precise and rapid method of measuring frequencies from 5 to 200 cycles per second. N. P. Case	237
196.	Coefficient of friction of fabrics. Alfred A. Mercier	243
197.	Accelerated tests of asphalts. O. G. Strieter	247
198.	Conductivity and density of chromic acid solutions. H. R. Moore and W. Blum	255
199.	Preliminary studies of the effect of dioxization and mold conditions on the tensile properties of carbon steel castings. J. V. McCrae and R. L. Dowdell	265
200.	The precipitation and ignition of magnesium ammonium phosphate. J. I. Hoffman and G. E. F. Lundell	279
201.	A new design of precision resistance standard. James L. Thomas	295
202.	The structure of the spectra of doubly and trebly ionized zirconium. C. C. Kiess and R. J. Lang	305
203.	Phase equilibria in the system Cr_2O_3-SiO_2. E. N. Bunting	325
204.	A method of measuring frictional coefficients of walkway materials. R. B. Hunter	329
205.	Bearing bronzes with additions of zinc, phosphorus, nickel, and antimony. E. M. Staples, R. L. Dowdell, and C. E. Eggenschwiler	349
206.	Cutting tests with cemented tungsten carbide lathe tools. T. G. Digges	365
207.	Heat transfer through metal-inclosed insulation. M. S. Van Dusen	385
208.	Effects of gases on photo-ionization of caesium by line absorption. F. L. Mohler and C. Boeckner	399
209.	A calorimetric determination of thermal properties of saturated water and steam from 0° to 270° C. N. S. Osborne, H. F. Stimson, and E. F. Fiock	411
210.	A review of calorimetric measurements on thermal properties of saturated water and steam. Ernest F. Fiock	481

BUREAU OF STANDARDS JOURNAL OF RESEARCH

CONTENTS OF RECENT NUMBERS

February, 1930 (Vol. 4, No. 2)

RP140. Standards for testing magnetic permeameters. Raymond Sanford. Price 5 cents.

RP141. Ultra-violet reflecting power of aluminum and several other metals. W. W. Coblentz and R. Stair. Price 5 cents.

RP142. The ring and ball method of test for softening point of bituminous materials, resins, and similar substances. Percy H. Walker. Price 5 cents.

RP143. Rayon as a paper-making material. Merle B. Shaw and George W. Bicking. Price 5 cents.

RP144. A precision method of calibrating a tuning fork by comparison with a pendulum. Charles Moon. Price 5 cents.

RP145. The principles of measurement and of calculation in their application to the determination of diophantine quantities. Edward W. Washburn. Price 10 cents.

RP146. Durability tests of spar varnish. C. L. Came. Price 5 cents.

RP147. A new dead-weight testing machine of 100,000 pounds capacity. L. B. Tuckerman, Herbert L. Whittemore, and Serge N. Petrenko. Price 5 cents.

RP148. Applying a visual double-modulation type radio range to the airways. H. Diamond. Price 10 cents.

RP149. The absorption of sound at oblique angles of incidence. P. R. Heyl, V. L. Chrisler, and W. F. Snyder. Price 5 cents.

RP150. Sensitivity of a galvanometer as a function of its resistance. H. B. Brooks. Price 5 cents.

RP151. Heat capacities in some aqueous solutions. Frederick D. Rossini. Price 5 cents.

March, 1930 (Vol. 4, No. 3)

RP152. Preliminary investigations upon two cellulosic wastes as sources for Xylose. W. L. Hall, C. S. Slater, and S. F. Acree. Price 5 cents.

RP153. Design of a portable temperature-controlled piezo oscillator. V. E. Heaton and W. H. Brattain. Price 5 cents.

RP154. A 12-course radio range for guiding aircraft with tuned reed visual indication. H. Diamond and F. G. Kear. Price 10 cents.

RP155. Applying the radio range to the airways. F. G. Kear and W. E. Jackson. Price 5 cents.

RP156. New piezo oscillations with quartz cylinders cut along the optical axis. August Hund and R. B. Wright. Price 20 cents.

RP157. Transverse tests of H-section column splices. James H. Edwards, H. L. Whittemore, and A. H. Stang. Price 10 cents.

RP158. Engine-ignition shielding for radio reception in aircraft. H. Diamond and F. G. Gardner. Price 15 cents.

RP159. Development of the visual type radiobeacon system. J. H. Dellinger, H. Diamond, and F. W. Dunmore. Price 20 cents.

Research papers are available as separates for purchase from the Superintendent of Documents United States Government Printing Office, Washington, D. C.

U. S. DEPARTMENT OF COMMERCE
R. P. LAMONT, Secretary
BUREAU OF STANDARDS
GEORGE K. BURGESS, Director

BUREAU OF STANDARDS JOURNAL OF RESEARCH

August, 1930
Vol. 5, No. 2

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1930

For sale by the Superintendent of Documents, Washington, D. C. - Price 40 cents; $2.75 Per Year on Subscription

For a partial list of previous research papers appearing in BUREAU OF STANDARDS JOURNAL OF RESEARCH, see pages 2 and 3 of the cover.

FIRE CLAYS; SOME FUNDAMENTAL PROPERTIES AT SEVERAL TEMPERATURES[1]

By R. A. Heindl and W. L. Pendergast

ABSTRACT

This report gives the results obtained in the second phase of an extensive investigation of fire-clay refractories. It is limited to the 26 representative clays included in that investigation. The geologic formation, chemical analyses, and pyrometric cone equivalents are given, together with such properties of the clays fired at two widely different temperatures, as porosity, shrinkage, thermal expansion, moduli of elasticity and rupture, and plastic flow. Data are given to show the conversion of aluminous fire clays into mullite and cristobalite by firing at certain temperatures. At higher temperatures the cristobalite is converted to glass.

CONTENTS

	Page
I. Introduction	213
II. Materials and identification	214
III. Preparation of specimens	215
IV. Methods of testing	216
1. Chemical analyses	216
2. Softening point test (pyrometric cone equivalent)	216
3. Thermal expansion	216
4. Modulus of elasticity, transverse strength, and plastic flow	216
5. Supplementary studies	216
V. Results	217
1. Chemical analyses	217
2. Tempering water and absorption of grog	217
3. Linear shrinkage and transverse strength	218
4. Porosity of bodies	219
5. Pyrometric cone equivalents	221
6. Linear thermal expansion	221
7. The effect of temperature of firing on the mineralogical composition of fire clays	226
8. Moduli of elasticity and transverse strength	231
9. Plastic flow	232
10. Grouping of clays	234
VI. Summary	236

I. INTRODUCTION

A report[2] was published during the past year giving the results of an extended study of fire-clay bricks, together with some preliminary test data of the fire clays used in their manufacture. In order that the present paper may contain all information obtained on the clays included in the present investigation, the data previously published will appear in this report, together with the results obtained in recent studies. The chemical analyses of the clays, pyrometric cone equivalent values and such physical properties as were determined after firing them at two widely different temperatures are given.

[1] This paper is the second of a series of reports which will be published on the general investigation of fire-clay refractories being conducted by this bureau.

[2] Progress Report on Investigation of Fire-Clay Bricks and the Clays Used in Their Preparation, B. S. Jour. Research, 3 (RP. 114); also J. Am. Ceram. Soc., 12 (10), pp. 640-675; 1929.

II. MATERIALS AND IDENTIFICATION

Twenty-six clays were furnished for this study by 12 manufacturers of refractory products. These clays were classed as follows: 7 flint, 4 semiflint, 12 plastic, and 3 miscellaneous. In addition, three samples of quartz and sand were included.

All clays supplied by any one manufacturer were given one letter of the alphabet and also a number following this letter to identify the various clays furnished by each company. Furthermore, letter identification of the clays in each case correspond with that assigned to the respective fire-clay bricks, for example, clays A–1 and A-2 are the clays supplied by the manufacturer of fire-clay brick having key letter "A" as given in the preceding report.[3]

The approximate location of the mines where the clays are produced and the geologic formation as furnished by the companies cooperating in this study and supplemented in some cases by State geologists are given briefly in Table 1.

TABLE 1.—*Type of clay, origin, and geologic formation*

Laboratory key	Type of clay	P. C. E.	Origin	Geologic age
A-1	Flint	32–33	Kentucky	Pottsville, Pennsylvanian formation.
A-2	Plastic	32	do	Do.
B-1	Semiflint	32–33	Pennsylvania	Conglomerate vein, Pottsville, Pennsylvanian formation.
B-2	Flint	33–34	do	Do.
B-3	Plastic	26	do	Middle Kittanning, Allegheny, Pennsylvanian formation.
C-1	Flint	33–34	do	Mercer vein, Pottsville, Pennsylvanian formation.
C-2	Plastic	28–29	do	Below Kittanning coal, Allegheny, Pennsylvanian formation.
D-1	Semiflint	32	Missouri	Near base of Cherokee, Pennsylvanian formation.
E-1	do	33	do	Do.
G-1	Plastic	33	New Jersey	Sedimentary formation, Raritan, cretaceous formation.
H-1	do	30	do	Raritan cretaceous formation.
H-2	do	33	do	Do.
H-3	Silica sand	32	do	Do.
H-4	do	32	do	Do.
H-5		33	do	Do.
H-6	Plastic	31	do	Do.
I-1	Semiflint	32–33	Kentucky	Pottsville, Pennsylvanian formation.
I-2	Flint	34	do	Do.
I-3	Plastic	30	Ohio	Clarion clay, Allegheny, Pennsylvanian formation.
K-1	Flint	34–35	Kentucky	Pottsville conglomerate, Pennsylvanian formation.
K-2	Plastic	32	do	Do.
M-1	Flint	34–35	Pennsylvania	Do.
M-2	Plastic	32	do	Do.
P-1	Crushed quartz.	33	California	
Q-1	Flint	33+	Missouri	Pennsylvanian formation.
R-1	Plastic	30–31	California	Ione Eocene Sedimentaries, Ione formation.
R-2	Kaolin	32–33	do	Residual deposit, Ione formation.
R-3	Siliceous	33	do	Sedimentary clay, Ione formation.
T-1	Plastic	30	Illinois	Beneath coal No. 1, Carbondale, Pennsylvanian formation, and above St. Peter sandstone, Ordovician series.

[3] See footnote 2, p. 213.

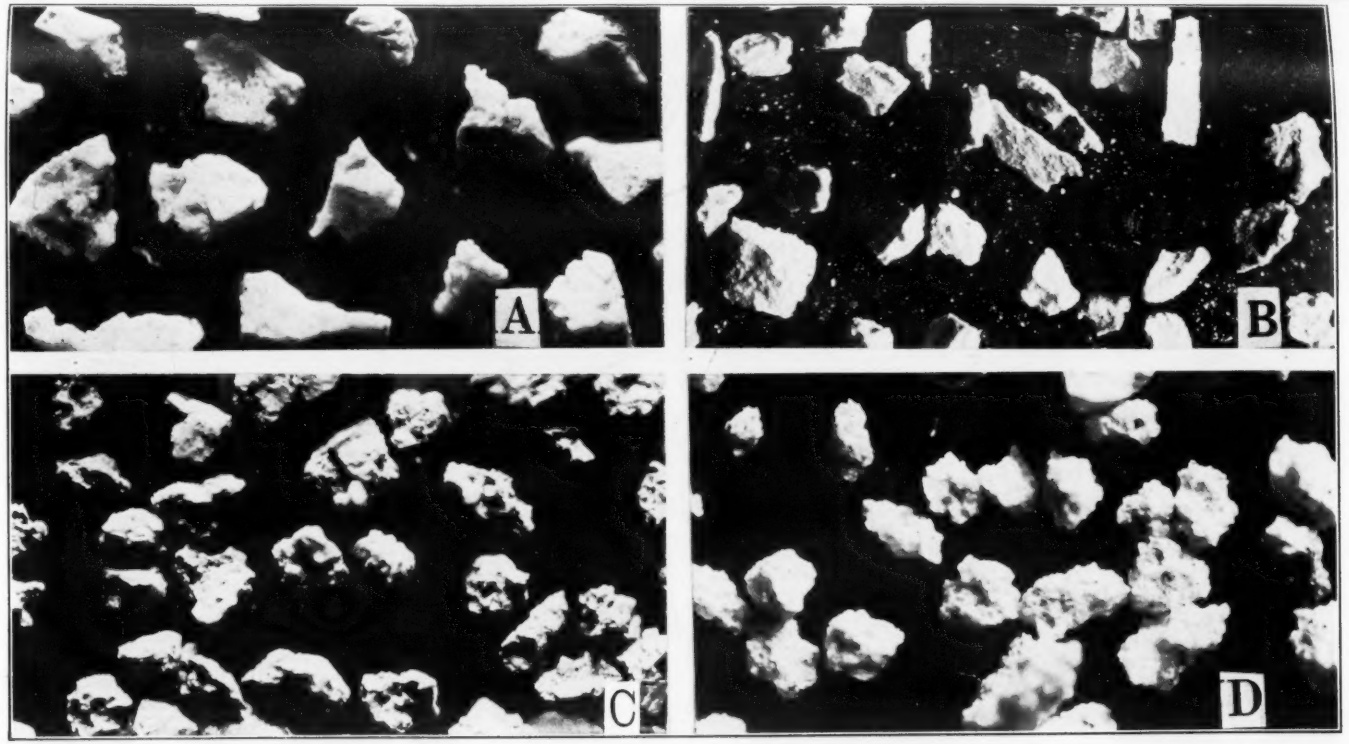


FIGURE 1.—*Photomicrograph (12 diameters) showing appearance of crushed grog prepared from four different fire clays*

The letters A, B, C, D identify the grogs with the description of the four groups given in the text.

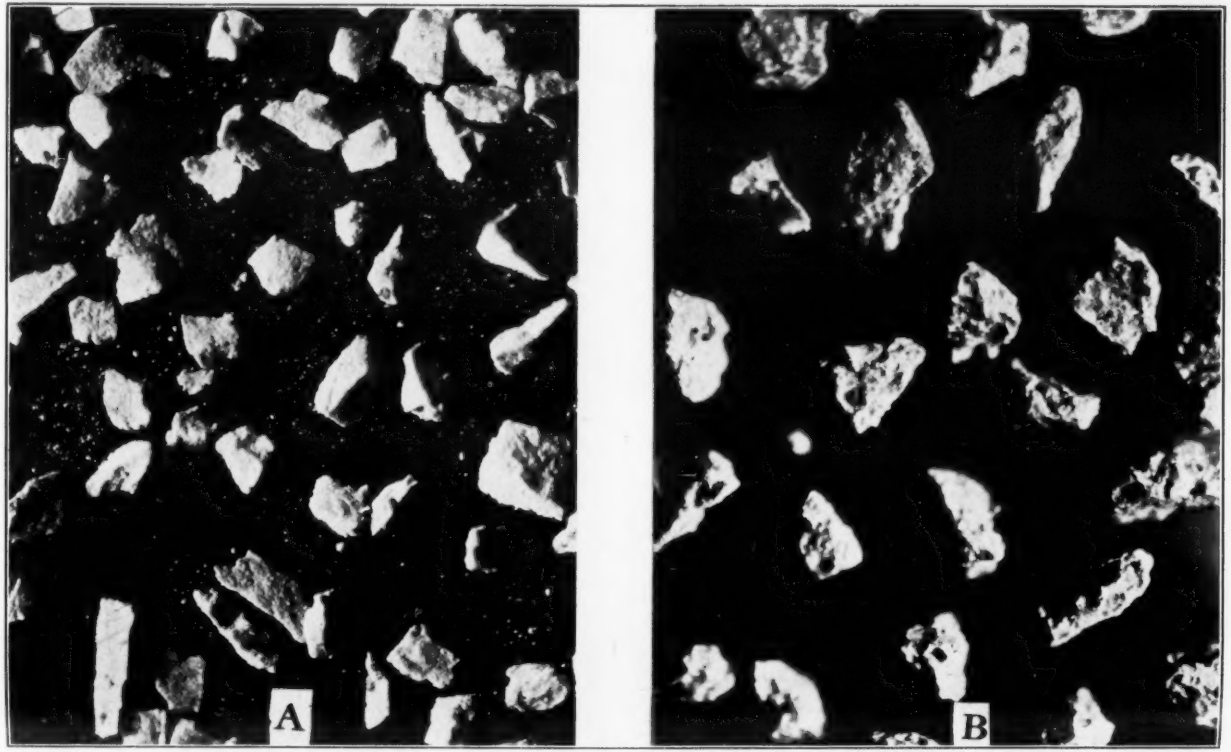


FIGURE 2.—*Photomicrograph (12 diameters) illustrating the effect of temperature of firing on the shape and fracture of the grog particle*

III. PREPARATION OF SPECIMENS

Two series of 26 different bodies were prepared. Each body contained only one raw clay and an equal amount of the same clay calcined (grog). The grog in the one series of bodies was fired at approximately 1,155° C. for three hours (cone 4 down) and the other series contained grog fired at 1,400° C. (cone 14 down) for the same length of time. Specimens of the clay bodies for obtaining experimental data were also fired at 1,155° C. and 1,400° C. for three hours. Those fired at 1,155° C. contained the grog fired at 1,155° C. and those fired at 1,400° C. contained the grog fired at 1,400° C. The grog was added as a part of the clay body in each instance to reduce warping of the specimens during drying and firing. In order to insure uniform and comparable results, the clay in each case was ground to pass a 100-mesh sieve, and the grog was crushed and graded into three sizes. The grog used in the bodies consisted of the following combination of sizes:

Percentage of each size	Sieve No. (U. S. standard series)	
	Passed—	Retained on—
50	20	40
25	40	100
25	100	Pan.

An examination of the crushed grogs indicated that, according to fracture and appearance, there are four general types. The characteristics of the individual particles in some cases are not clearly defined, but most of the grogs could be classified according to the following groups:

(*a*) More or less regular in shape with comparatively sharp cleavage faces.

(*b*) More or less regular in shape with a tendency to have a platy fracture.

(*c*) Irregularly shaped without sharp fractures.

(*d*) Slightly rounded and somewhat soft.

A photomicrograph of a sample of grog representing each of the foregoing groups is given in Figure 1. The effect of temperature of firing on the fracture or cleavage and general appearance of a grog (R-1) is illustrated in the photomicrograph given in Figure 2.

Eight specimens, 1 by 1 by 12 inches, and six specimens, 1 by 1 by 6 inches, were prepared from each of the 52 bodies. The 12-inch specimens were used for modulus of elasticity and transverse strength determinations and the 6-inch specimens for obtaining such properties as "tempering" or "conditioning" water, linear shrinkage, and dry strength. Data referred to in this report relative to absorption of grog, chemical analyses, pyrometric cone equivalent values, and mineralogical changes of clays fired at certain temperatures were obtained on the clays alone, and data on the other properties studied were obtained on the specimens containing equal parts of clay and grog.

FIGURE 2.—Photomicrograph (12 diameters) illustrating the effect of temperature of firing on the shape and fracture of the grog particle.

IV. METHODS OF TESTING

1. CHEMICAL ANALYSES

In making the chemical analyses of the fire clays the procedure followed was, in general, the method of analysis for refractories described by Lundell and Hoffman.[4]

2. SOFTENING POINT TEST (PYROMETRIC CONE EQUIVALENT)

The softening point (P. C. E.) test was carried out according to the method approved by the bureau, and known as the A. S. T. M. standard method, serial designation C24–20.[5]

3. THERMAL EXPANSION

Linear thermal expansions of the fire clays were determined by a direct method [6] on specimens measuring approximately 1 by 1 by 6 inches and which had been fired at 1,155° C. and at 1,400° C. Determinations were made from 20° [7] to 1,000° C.

4. MODULUS OF ELASTICITY, TRANSVERSE STRENGTH, AND PLASTIC FLOW

A detailed description of the apparatus used in observing deflections of the specimens under various loads, the determination of the transverse strength (modulus of rupture), and the method for determining the load-deflection curves were published in the Third Progress Report of the Sagger Investigation.[8] The modulus of elasticity and modulus of rupture were determined at several temperatures, the former from the load-deflection curve and the latter using the load which broke the specimen.

The plastic flow at 1,000° C. of the various fire-clay bodies was determined with the same apparatus as was used to determine the elasticity and breaking strength. The plastic flow of the material under any particular stress increment was considered as the "set" or difference between the deflection caused by the load and the recovery of the material on removal of this load. A detailed description of the method for determining this property was given in the Fourth Progress Report of the Sagger Investigation.[9]

5. SUPPLEMENTARY STUDIES

Linear drying shrinkage and dry strength were determined on the 6-inch specimens of the fire-clay bodies after drying for several days at atmospheric temperature and finally at approximately 110° C. for 24 hours and cooling in a desicator. Linear burned shrinkage was obtained from specimens fired at 1,155° and 1,400° C. These specimens were fired at the same time as those on which the other test data were determined.

---

[4] Analysis of Bauxite and of Refractories of High Alumina Content, B. S. Jour. Research, **1** (RP5); July, 1928.
[5] Described in Am. Soc. Testing Materials Standards for 1927, Pt. II, p. 151.
[6] For a description of the apparatus and method used, see J. Am. Ceram. Soc., **9** (9), pp. 555–574; 1926.
[7] Room temperature was approximately 20° C. during these experiments.
[8] J. Am. Ceram. Soc., **10** (7), pp. 524–534; 1927.
[9] J. Am. Ceram. Soc., **10** (12), pp. 995–1004; 1927.

The water porosity was determined by treating the specimens in a vacuum for one hour at an absolute pressure of 6 mm of mercury. Distilled water was added while the specimens were still in vacuum and then boiled in vacuum for one and one-half hours. The specimens remained under water an additional 18 hours before being weighed.

V. RESULTS

1. CHEMICAL ANALYSES

The chemical analyses of the materials investigated are given in Table 2. A study of the data shows a wide variation in composition Samples H–3, H–4, and P–1 [10] (Table 2) are composed largely of silica. On the other hand, fire clays K–1, M–1, and Q–1 have a composition which closely approaches that of kaolin containing very little free quartz, and are here referred to as "aluminous."

TABLE 2.—*Chemical analyses of fire clays*

Laboratory key letter	Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Total
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A-1	14.30	43.32	35.72	3.26	2.02	0.18	0.40	99.20
A-2	14.08	44.64	35.84	2.39	1.77	.26	.52	99.50
B-1	13.26	43.38	37.97	1.39	2.12	----------	.31	98.43
B-2	14.58	43.06	37.84	2.14	1.84	.12	.04	99.62
B-3	8.16	58.68	24.95	2.39	1.70	.19	.70	96.77
C-1	13.78	42.74	39.18	1.01	2.33	----------	.29	99.33
C-2	10.86	50.38	30.87	2.56	2.27	.32	.30	97.56
D-1	12.34	51.82	32.09	1.24	1.63	----------	.58	99.70
E-1	14.06	45.98	37.12	.88	1.90	.12	.29	100.35
G-1	14.32	47.09	36.25	.75	1.89	.44	.06	100.80
H-1	7.42	70.29	19.46	.88	2.02	.22	.03	100.32
H-2	14.36	46.36	35.43	1.87	1.57	.44	.46	100.50
H-3	1.62	91.52	4.65	.28	.67	.26	.31	99.31
H-4	2.86	87.68	7.33	1.06	1.25	.38	.14	100.70
H-5	12.82	52.26	32.30	.84	1.72	.26	.02	100.02
H-6	8.14	68.20	21.37	.78	1.63	.34	.12	100.58
I-1	11.62	51.42	32.80	.93	2.33	----------	.52	99.62
I-2	13.66	44.66	37.58	1.33	1.53	.66	.15	99.67
I-3	10.62	53.50	29.82	1.95	1.73	.23	.16	98.01
K-1	14.86	42.50	39.68	.76	2.34	----------	.12	100.26
K-2	12.28	47.00	33.41	2.59	2.00	.48	.32	98.08
M-1	13.68	44.56	38.19	1.12	2.21	.14	.10	100.00
M-2	11.46	45.76	35.67	1.95	1.72	.30	.64	97.50
P-1	.28	97.48	.72	.14	.46	.16	.32	99.56
Q-1	13.32	42.32	39.63	.84	1.81	.68	.50	99.10
R-1	12.06	52.78	29.90	2.37	1.07	.04	1.20	99.42
R-2	14.66	44.46	37.31	1.13	2.76	.20	.12	100.64
R-3	7.22	72.78	18.94	.65	.61	.23	.14	100.57
T-1	10.92	60.26	25.28	1.62	1.28	.38	.16	99.90

2. TEMPERING WATER AND ABSORPTION OF GROG

The tempering water—that is, the percentage of water considered as desirable for securing proper molding consistency of the clay test specimens—is given in Table 3. This information is given for those specimens containing grog fired to cone 4 as well as for those containing grog fired to cone 14.

[10] Complete test data on materials H–3, H–4, and P–1 were not obtained because they are largely silica.

The percentage absorption of the grog fired at the two temperatures is also given in Table 3. The data on absorption show only two clays (B–3 and C–2) overfired at cone 14. It may be that other clays are overfired, but this is not indicated by their appearance, and since no burns were made between cones 4 and 14, it is not known whether any of the clays reached an absorption lower than that given in the table. The smallest change in absorption was shown by the grog prepared from the highly siliceous clays.

TABLE 3.—*Tempering water of fire clay bodies and absorption of grogs used*

Laboratory key	Tempering water; specimens containing grog fired to—		Absorption (per unit weight); grog fired to—	
	Cone 4	Cone 14	Cone 4	Cone 14
	Per cent	*Per cent*	*Per cent*	*Per cent*
A-1	17.3	16.1	11.6	9.4
A-2	18.1	16.0	10.6	.9
B-1	18.1	19.1	12.3	7.4
B-2	18.9	17.4	16.7	1.1
B-3	17.3	16.1	7.8	12.0
C-1	21.4	16.7	16.0	11.6
C-2	16.5	16.7	6.0	8.7
D-1	18.1	14.5	7.7	3.6
E-1	18.8	14.9	13.8	2.6
G-1	23.9	16.9	26.3	6.3
H-1	20.9	19.7	20.7	18.1
H-2	22.0	19.3	9.6	2.6
H-5	24.8	18.4	20.9	6.8
H-6	20.1	19.7	20.0	17.5
I-1	18.1	14.8	13.0	6.8
I-2	18.1	14.8	14.6	6.7
I-3	18.7	15.1	11.5	1.1
K-1	20.5	16.6	17.6	11.1
K-2	19.4	17.2	7.9	.4
M-1	20.8	18.1	19.7	11.7
M-2	19.2	17.2	22.3	6.9
Q-1	18.1	16.6	10.7	4.5
R-1	20.1	19.4	10.4	5.5
R-2	22.3	18.3	9.2	1.4
R-3	26.8	28.5	26.1	22.5
T-1	16.4	15.3	7.9	6.5

The absorption of the grog apparently has little effect on the amount of tempering water used in preparing the specimens. Clay B–2 may be cited as a typical example. The percentage absorption decreased approximately 15.5 between the cone 4 and cone 14 firing, but the difference in percentage tempering water was only 1.5.

3. LINEAR SHRINKAGE AND TRANSVERSE STRENGTH

The linear shrinkage and strength after drying and the total linear shrinkage after firing of the specimens prepared with grog fired at the two different temperatures are given in Table 4.

TABLE 4.—*Dry and fired shrinkage, and strength of fire-clay bodies*

Laboratory key	Linear drying shrinkage		Total fired shrinkage		Dry strength (cross breaking)	
	Specimens containing grog fired to—					
	Cone 4	Cone 14	Cone 4	Cone 14	Cone 4	Cone 14
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Lbs./in.²*	*Lbs./in.²*
A-1	3.7	4.4	8.3	7.3	225	145
A-2	3.4	4.6	7.2	8.3	155	145
B-1	3.0	3.2	6.5	12.5	90	80
B-2	2.6	4.9	5.0	6.9	60	70
B-3	3.0	3.8	9.0	6.9	140	150
C-1	3.1	5.6	6.7	7.9	55	60
C-2	3.1	3.8	8.0	8.5	205	245
D-1	3.6	4.0	7.3	7.4	195	195
E-1	3.2	3.8	8.9	7.4	190	165
G-1	2.8	3.6	9.3	6.6	120	140
H-1	3.0	4.4	4.3	2.2	100	135
H-2	3.4	4.2	9.7	4.3	165	200
H-5	3.2	4.2	8.5	3.7	190	140
H-6	2.4	4.2	4.6	2.3	85	120
I-1	2.7	4.4	5.5	7.7	110	110
I-2	3.5	4.8	5.8	6.9	180	105
I-3	3.9	4.6	8.8	7.9	225	215
K-1	3.9	5.2	8.1	7.1	60	70
K-2	4.2	5.6	9.2	9.2	180	225
M-1	3.0	6.8	6.7	8.6	55	80
M-2	3.5	4.8	9.1	9.5	80	105
Q-1	4.2	4.8	8.7	9.3	180	180
R-1	4.2	5.4	9.8	9.7	180	375
R-2	2.5	3.8	13.1	7.5	85	125
R-3	3.5	6.0	7.4	7.9	35	70
T-1	3.4	5.4	5.3	6.3	400	295

The majority of specimens containing grog fired at the higher temperature show greater dry strength in comparison to those containing grog fired to the lower temperature, but the average values do not show a significant difference. The data on fired shrinkage do not indicate that any of the bodies are overfired at 1,400° C. The bodies made up of clays H–1, H–5, and H–6, however, show a negative shrinkage (expansion) which is due to their high silica content and represents the conversion of the quartz to cristobalite. As in the case of the porosity determinations the data obtained on fired shrinkage are quite misleading as an indication of whether the bodies are overfired because it is not known whether they reached their minimum shrinkage at some temperature before 1,400° C. In the case of body B–3, an examination shows it to be overfired, although the shrinkage measurements do not so indicate.

4. POROSITY OF BODIES

The porosities of the fired specimens were determined on sections cut from the ruptured 12-inch bars on which data were obtained for moduli of elasticity and rupture computations. The results obtained

on specimens fired at 1,155° C. are given in Table 5 and those fired at 1,400° C. in Table 6. The porosity values given represent the average of not less than three determinations.

TABLE 5.—*Modulus of elasticity, transverse strength, and porosity of fire clays fired at 1,155° C. for three hours*

Laboratory key letter	Tested at 20° C.		Tested at 550° C.		Tested at 1,000° C.		Porosity
	Modulus of—		Modulus of—		Modulus of—		
	Rupture	Elasticity	Rupture	Elasticity	Rupture	Elasticity	
	Lbs./in.²	*1,000 lbs./in.²*	*Lbs./in.²*	*1,000 lbs./in.²*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*
A-1	2,755	5,530	2,745	5,275	3,925	1,040	23.6
A-2	2,415	3,840	2,070	3,785	2,110	595	27.3
B-1	1,690	3,000	2,055	4,490	1,950	505	28.3
B-2	480	835	580	1,270	375	205	35.1
B-3	3,370	7,625	3,555	7,540	(1)	660	9.2
C-1	825	1,515	790	1,635	650	305	35.4
C-2	3,220	7,135	2,775	5,610	(1)	270	20.2
D-1	2,435	3,945	2,415	4,200	2,940	945	25.5
E-1	3,205	5,115	3,250	6,260	3,240	1,610	21.2
G-1	1,320	1,890	2,100	2,525	2,760	1,040	33.3
H-1	565	584	795	1,075	925	555	37.4
H-2	2,010	3,575	2,655	4,905	3,290	1,010	29.1
H-5	1,100	1,535	1,640	2,020	1,610	905	35.5
H-6	465	410	675	840	740	415	37.2
I-1	1,185	1,725	1,485	2,785	2,160	535	30.3
I-2	945	2,000	1,010	2,080	850	295	32.7
I-3	2,570	5,005	3,160	5,385	4,300	715	20.4
K-1	825	1,650	820	1,690	825	800	31.4
K-2	2,710	6,075	2,385	5,595	2,770	400	24.7
M-1	870	1,695	1,040	1,855	990	245	33.1
M-2	2,795	5,700	2,690	5,705	3,665	465	24.7
Q-1	2,235	4,310	2,500	4,390	1,480	620	27.3
R-1	2,450	4,730	2,645	5,675	4,015	730	25.9
R-2	2,075	4,305	2,335	4,550	2,390	1,515	22.0
R-3	490	505	680	760	1,100	590	41.2
T-1	1,835	2,595	1,950	3,515	3,140	1,180	28.0

[1] Specimen did not rupture.

TABLE 6.—*Modulus of elasticity, transverse strength, and porosity of fire clays fired at 1,400° C. for three hours*

Laboratory key letter	Tested at 20° C.		Tested at 550° C.		Tested at 1,000° C.		Porosity
	Modulus of—		Modulus of—		Modulus of—		
	Rupture	Elasticity	Rupture	Elasticity	Rupture	Elasticity	
	Lbs./in.²	*1,000 lbs./in.²*	*Lbs./in.²*	*1,000 lbs./in.²*	*Lbs./in.²*	*1,000 lbs./in.²*	*Per cent*
A-1	2,750	5,800	2,780	6,180	3,060	1,930	24.7
A-2	2,765	6,570	2,745	7,415	3,580	1,425	19.7
B-1	2,160	5,060	2,200	5,320	2,250	940	24.7
B-2	635	1,485	725	1,865	705	645	31.1
B-3	2,285	6,720	3,240	8,470	2,750	300	.7
C-1	1,060	2,290	2,325	2,745	1,585	990	25.6
C-2	2,630	8,175	3,000	8,785	5,150	850	11.1
D-1	3,625	7,420	2,985	7,960	3,590	2,655	16.8
E-1	2,240	5,820	3,190	7,015	2,800	2,410	21.8
G-1	1,960	3,090	2,170	4,025	2,295	2,160	27.4
H-1	670	795	1,020	1,730	1,575	1,480	34.0
H-2	2,745	6,980	2,995	7,220	3,120	1,740	24.7
H-5	2,200	3,310	2,080	3,645	2,545	2,285	28.0
H-6	695	695	880	1,335	1,430	1,240	33.4
I-1	2,205	3,835	2,735	6,290	3,060	2,400	26.7
I-2	1,500	2,940	1,625	3,490	1,850	985	27.7
I-3	3,145	8,830	2,945	9,425	3,790	905	12.8
K-1	1,155	2,405	1,155	2,655	1,030	1,310	30.1
K-2	2,990	7,460	2,480	7,785	2,970	1,070	17.0
M-1	850	2,040	830	2,335	1,140	790	30.2
M-2	2,895	6,435	2,515	6,325	3,080	890	20.3
Q-1	2,685	5,885	2,355	5,870	3,170	1,020	22.0
R-1	3,210	7,655	3,090	8,960	3,450	1,375	17.2
R-2	1,865	4,065	1,815	4,300	2,030	2,300	30.6
R-3	475	465	575	875	750	670	37.9
T-1	2,230	3,590	2,490	5,345	3,140	2,790	25.7

5. PYROMETRIC CONE EQUIVALENTS

The P. C. E. values for all the materials included in this study are given in Table 1 and, with the exception of samples B–3 and C–3 (Pennsylvania plastic fire clays), have a P. C. E. value of 30 or above.

6. LINEAR THERMAL EXPANSION

The linear thermal expansions of the 26 fire-clay bodies were determined from atmospheric temperature to 1,000° C. Determinations were made on the clays after having been fired at 1,155° C. and also at 1,400° C. Check expansion determinations were made of all specimens, and the greatest variation in the data obtained on the same body was less than ±2.5 per cent.

The average coefficients of linear expansion for several different temperature ranges are given in Table 7. These values are given to show how misleading it may be to accept the average coefficient of expansion from 20° to 1,000° C. as expressing the true thermal expan-

sion behavior of the clay on heating, since it gives no indication of the volume changes which may occur over short temperature ranges. For example, the coefficient of expansion from 20° to 1,000° C. for clay B–2 gives no intimation that the material expands much more rapidly between 100° and 200° C. (fig. 4) than between 200° and 1,000° C. The data given show the effect on the thermal expansion of firing the clays at two widely different temperatures and also how great the differences in this property may be over certain temperature ranges.

TABLE 7.—*Coefficient of linear thermal expansion of fire clays fired at two different temperatures*

Laboratory key letter	Average coefficient of expansion [1] for temperature range (° C.)						Classed in group [2]
	100–200		500–600		20–1,000		
	Clays fired at (° C.)—						
	1,155	1,400	1,155	1,400	1,155	1,400	
A–1	12.6	13.2	6.5	5.6	6.3	6.3	2
A–2	10.7	5.0	6.2	5.0	5.9	4.9	1
B–1	7.4	4.2	5.8	4.2	5.4	4.3	1
B–2	12.5	16.8	5.5	5.6	6.1	6.5	2
B–3	4.2	3.7	6.4	4.4	5.4	4.4	3
C–1	10.7	11.1	5.8	5.0	6.1	6.0	2
C–2	5.3	3.6	5.8	4.5	5.2	4.4	3
D–1	16.5	19.8	8.2	6.7	6.6	7.4	4
E–1	13.0	16.0	7.1	5.5	6.2	6.7	4
G–1	11.5	18.7	9.1	7.5	6.3	6.8	4
H–1	16.0	25.0	20.6	12.3	7.8	7.6	4
H–2	10.9	6.3	6.3	5.2	5.9	5.2	1
H–5	15.5	19.9	10.0	7.5	6.8	7.2	4
H–6	16.0	28.2	19.7	10.0	7.5	7.8	4
I–1	13.1	16.1	10.0	7.4	6.3	6.6	4
I–2	11.1	12.2	5.6	5.5	6.1	6.4	2
I–3	7.0	3.7	8.2	4.6	5.4	4.1	1
K–1	10.8	17.5	6.0	5.3	6.6	7.0	2
K–2	5.4	3.4	6.6	4.7	5.3	4.6	3
M–1	4.0	12.9	4.7	5.2	4.8	6.3	5
M–2	4.0	4.2	5.1	5.0	5.1	5.0	5
Q–1	5.3	4.6	6.1	5.1	5.6	5.2	3
R–1	9.6	6.2	6.2	4.4	5.8	4.9	1
R–2	12.0	17.6	6.2	5.9	6.7	6.8	2
R–3	8.0	21.0	12.7	12.0	5.4	7.0	4
T–1	21.3	30.0	11.9	5.6	8.1	8.0	4

[1] Values to be multiplied by 10^{-6}.
[2] These groups correspond to those referred to in section 6, "Linear Thermal Expansion."

The various clays may be classified into five groups, according to their thermal expansion characteristics as determined by the free silica present either as quartz or in one or more of its allotropic modifications.

Group 1.—Five bodies (A–2, B–1, H–2, I–3, and R–1) after being fired at 1,155° C., show a high rate of expansion below 200° C. and a somewhat less and more uniform rate between approximately 200° and 1,000° C. The data indicate that any free silica present is

probably either in the form of tridymite or cristobalite. The expansion data obtained on these clays after firing at the higher temperature showed that the rate of expansion was practically uniform throughout the entire temperature range, indicating that the cristobalite had been converted to a highly siliceous glass. Body I–3, after the firing at 1,155° C., in addition to the expansion characteristics described, shows also an increased rate of expansion between 500° and 600° C. caused by the inversion of the alpha to beta quartz. After firing at 1,400° C. this body shows a slight increase in the rate between approximately 750° and 850° C. Examples of the expansion characteristics of this group are given in Figure 3 and represent the data obtained on specimens of bodies H–2 and I–3.

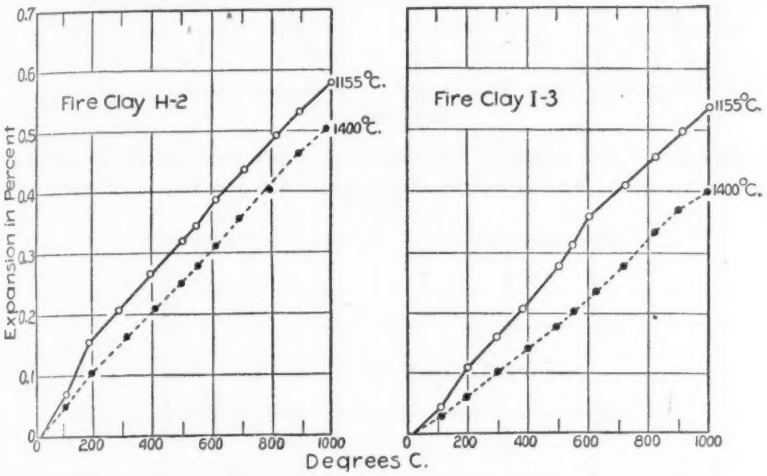


FIGURE 3.—*The expansion characteristics of fire clays classed in Group 1*
The curves show that the thermal expansion of these clays decreases by firing at the higher temperature

Group 2.—Six clays (B–2, I–2, K–1, R–2, A–1, and C–1) in this group are characterized by a high rate of expansion below 200° C. occurring not only in test specimens fired at 1,155° C., but also after having been fired at 1,400° C. The first four clays show a higher expansion after the 1,400° C. firing when compared with that obtained on the specimens fired at 1,155° C. The increased total expansion is caused by the increased rate of expansion below 200° C., as shown by the greater inflection of the curve below that temperature.

The expansions of the other two clays, namely, A–1 and C–1, were practically unchanged by the firing at the higher temperature. The expansion data indicate that any free silica present in these fired clays occurs as either tridymite or cristobalite. The expansions are illustrated by the curves, given in Figure 4, representing data obtained on clays B–2 and C–1.

Group 3.—Four clays (B–3, C–2, K–2, and Q–1) after the firings at both 1,155° and 1,400° C. have a comparatively uniform rate of expansion from room temperature to 1,000° C., with the exception of a slight increase in the rate between approximately 750° and 850° C. of the clay specimens fired at 1,400° C. The test pieces

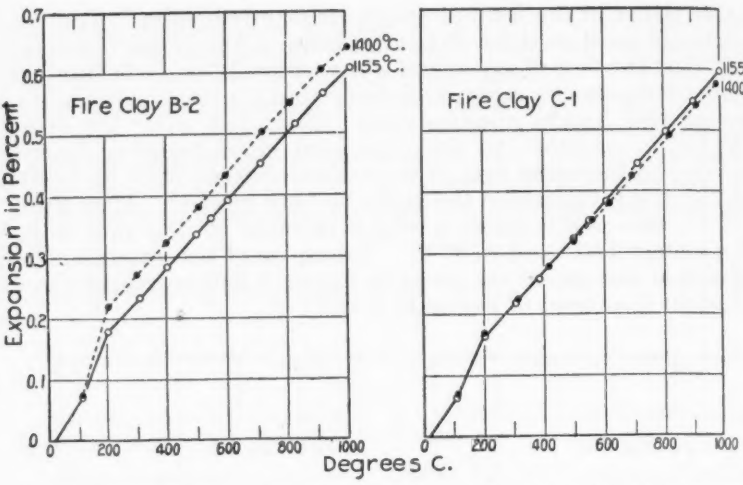


FIGURE 4.—*The expansion characteristics of fire clays classed in group 2*

The curves for clay B-2 show that the expansion has increased after firing at the higher temperature

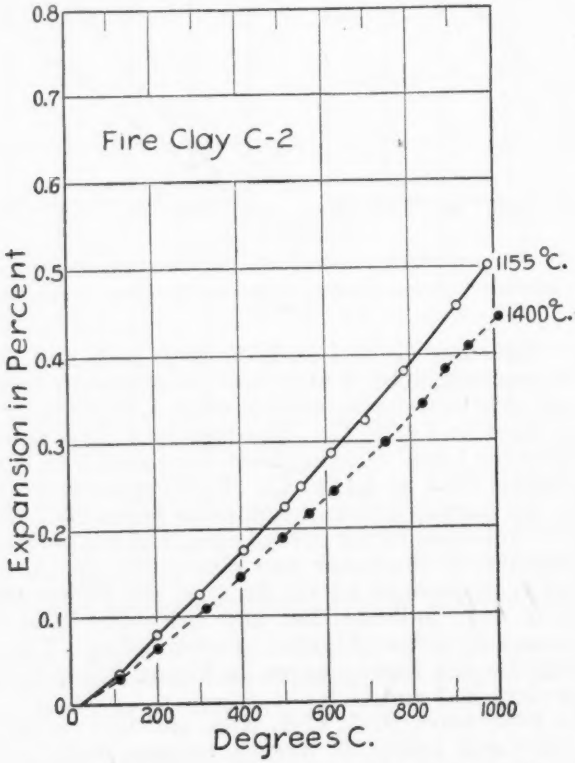


FIGURE 5.—*Thermal expansion chacteristics of clays classed in group 3 are shown by the data obtained on clay C–2*

fired at the higher temperature show a considerably lower total expansion compared with those fired at the lower temperature. The expansion data obtained on clay C–2 illustrating this group are shown by the curves in Figure 5.

Group 4.—Nine clays (D–1, E–1, G–1, H–1, H–5, H–6, I–1, T–1, and R–3) after firing at 1,155° C. have a high rate of expansion below 200° C. and also between approximately 540° and 600° C. These curves show that quartz, cristobalite, and tridymite are probably all present in the clay bodies. After firing at 1,400° C. the inflection just below 600° C. present in the expansion curves obtained after firing the specimens at 1,155° C. has practically disappeared or is greatly reduced. The total expansion, however, has increased in some cases due to the conversion of the quartz into cristobalite. Although R-3 may not strictly belong in this group because of the nature of

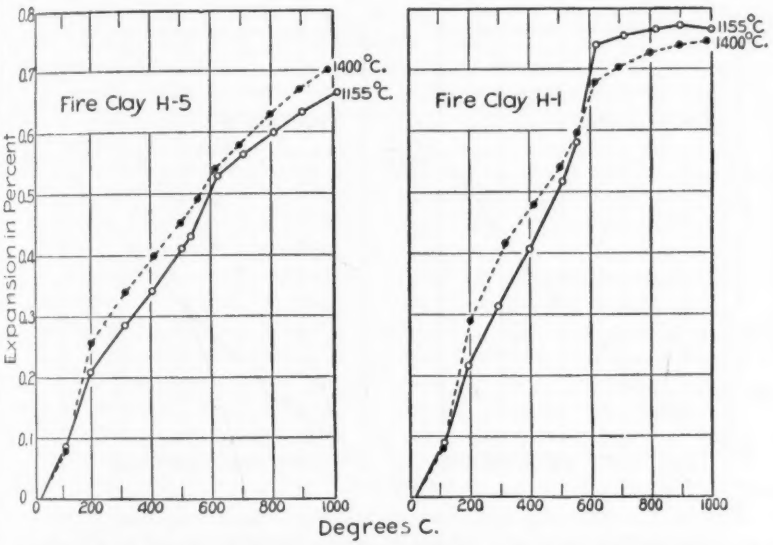


FIGURE 6.—*The thermal expansion curves of clays H–5 and H–1 representative of clays in Group 4*

The clays are of the highly siliceous type and as indicated by the curves are especially rich in cristobalite after firing at 1,400° C.

its expansion after having been fired at 1,155° C., it is included because the expansion shown after firing at 1,400° C. is very similar to that of the other clays. The expansion data of clays H–1 and H-5, are shown by the curves in Figure 6. The continued high rate of expansion after firing at 1,400° C. is undoubtedly partially due to the high silica content and to the fact that the free quartz is present in comparatively coarse grains.[11]

Group 5.—The two remaining bodies, M–2 and M–1, have individual expansion characteristics and can not readily be classed in any of the foregoing groups. Body M–2 has a uniform rate of expansion

[11] Otto Bartsch calls attention to the effect of firing temperature and firing time on transformation of quartz of varying grain size in his paper Expansion Behavior of Some Quartz Containing Clays, Glastech. Ber., 7 (2), pp. 48–61; 1929.

from approximately 20° to 1,000° C. It is the only clay body of all those tested which shows no change in the rate of expansion after having been fired at 1,400° C. in comparison with that obtained after the 1,155° C. firing. The expansion curves for this body are shown in the left section of Figure 7.

The expansion data obtained on body M–1 fired at 1,155 ° C. indicate the rate to be uniform from 20° to 1,000° C. The total expansion of the material after having been fired at 1,400° C. has increased decidedly over that obtained after having been fired at 1,155° C. This change in total expansion is caused entirely by the high rate occurring below 200° C., due undoubtedly to the presence of either or both cristobalite and tridymite. The probable reaction resulting in the formation of this cristobalite and tridymite is discussed under section 7. Curves for body M–1 are given on the right in Figure 7.

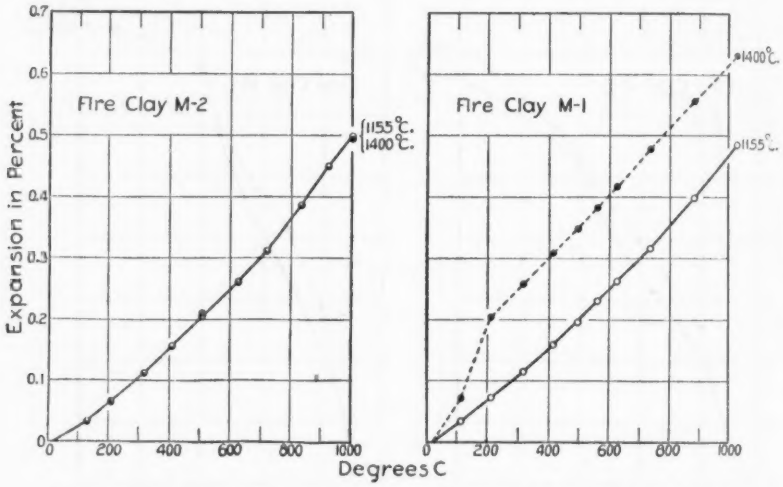


FIGURE 7.—*The clays referred to in this figure have individual expansion characteristics and can not be readily classed in any of the groups illustrated*

Clay M–2 apparently has the same rate of expansion whether fired at 1,155° or 1,400° C., whereas clay M–1 shows a decided change in this property

7. THE EFFECT OF TEMPERATURE OF FIRING ON THE MINERALOGICAL COMPOSITION OF FIRE CLAYS

It has been known for some time that mullite and free silica develop during the firing of clays in certain temperature ranges and that fluxes bear an important relation to that development. As a result of the present study it is possible to show how the linear thermal expansion is directly affected by the formation of mullite and the development of free silica accompanying it.

Five clays, namely, B–2, C–1, I–2, K–1, and M–1, whose alumina-silica ratio closely approaches that of kaolin and which contain little, if any, free quartz, were found to be especially sensitive to heat treatment. Firing at certain temperatures caused marked changes in their mineralogical composition. This is indicated by linear thermal expansion measurements and to a lesser extent by petro-

graphic examination. There are other clays included in this investigation whose compositions are probably affected in the same manner as the above five clays, but this particular phase of the study was limited to these five clays.

The formation of mullite from clay may be expressed as follows:

$$3(Al_2O_3.2SiO_2) + \text{heat} = 3Al_2O_3.2SiO_2 + 4SiO_2$$

Thermal expansion measurements were made after firing the clays at progressively increasing temperatures to show how the change in composition proceeds in accordance with the above equation. Petrographic examinations [12] were made of the raw clays and also after each firing treatment.

Expansion measurements from 20° to 900° C. were made with the interferometer [13] on specimens of clays C–1, K–1, and M–1 fired to cone 5 half down (1,120° C.); cone 6 (1,180° C.); cone 11 (approximately 1,260° C.); cone 15 half down (1,400° C.); and cone 19 (1,525° C.). Curves showing the data obtained on these three clays are given in Figure 8. Measurements were made on specimens of clays B–2 and I–2 only after firing at three temperatures, and data regarding them are not included.

The expansion curves (fig. 8) obtained on each of the clays after firing at 1,120° C. show the rate of expansion to be uniform from 20° to 900° C. Expansion measurements made on the clays after firing at 1,525° C. also show the rate of expansion to be uniform, but slightly below that obtained on specimens fired at the lower temperature in the case of C–1 and K–1, but decidedly lower in the case of M–1, as may be seen from the curves in Figure 8. The changes occurring in both the mineralogical composition and thermal expansion characteristics of the materials when fired at temperatures between 1,120° and 1,525° C. are quite decided, as indicated both by the results of the petrographic examination and by the expansion curves given in Figure 8. A description of these changes follows:

Clay C–1.—*Fired at 1,120° C.*—Rate of expansion uniform from 20° to 900° C. The petrographic examination shows the clay to be wholly converted to an isotropic, probably amorphous material with a mean index of refraction of 1.57. This serves as a matrix for minute particles which are birefringent and have a very different index from the amorphous material.

Fired at 1,180° C.—The total expansion after firing at 1,180° C. has increased appreciably from 20° to 200° C. when compared with that obtained after firing at 1,120° C. This change in expansion is caused by the partial formation of mullite from the clay with the liberation of silica in accordance with the above equation. The change in the rate of expansion below 200° C. indicates that the silica which is set free (excess silica) is probably present as cristobalite.

Fired at 1,260° C.—The maximum total expansion both at 200° and 900° C. was obtained after firing at 1,260° C. At 200° C. the total expansion has increased over 150 per cent and at 900° C. about 35 per cent when compared with that obtained at the same temperatures on the specimen fired at 1,120° C. From the data obtained

[12] Petrographic examinations made by H. Insley.
[13] Described in B. S. Sci. Paper No. 485.

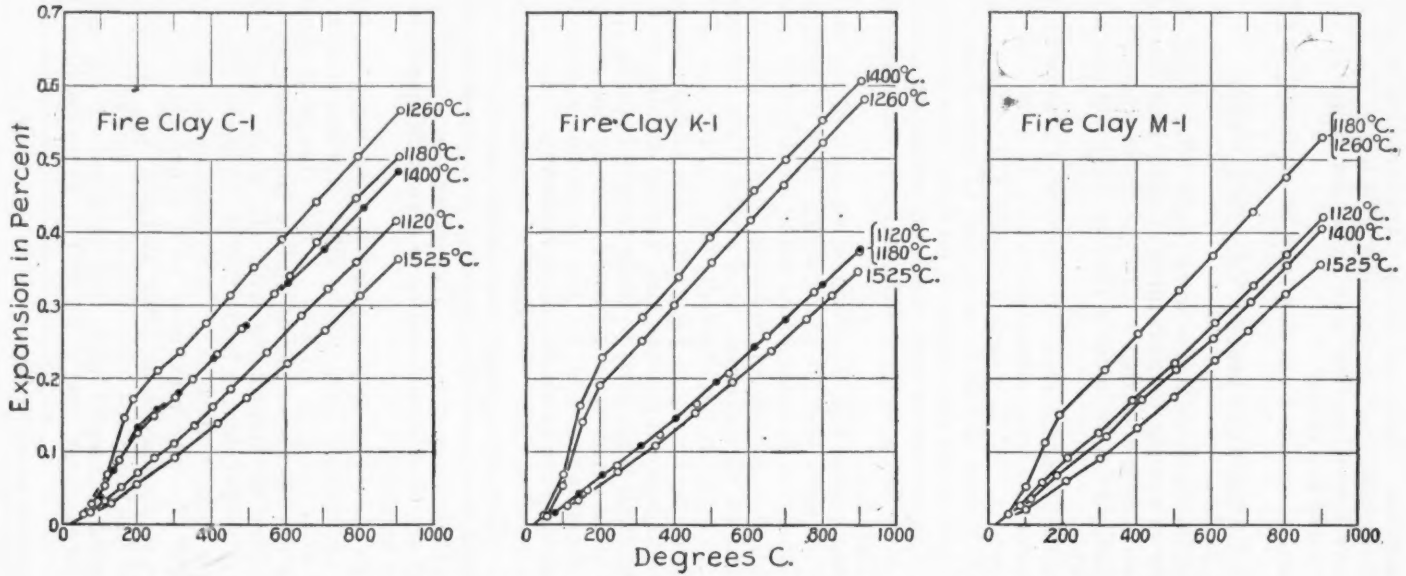


FIGURE 8.—*Linear thermal expansions of aluminous fire clays after firing at each of five different temperatures*

The development of cristobalite, mullite, and glass at various stages is indicated

it would appear that the formation of mullite from the clay is about complete.

Fired at 1,400° C.—A decided decrease in the expansion between 20° and 200° C. has taken place. The curve obtained practically coincides with that obtained after firing the clay at 1,180° C. This indicates that the crystalline silica (cristobalite) has partially been converted to a highly siliceous glass. The petrographic examination shows only two substances present: (*a*) Minute needles of mullite with a maximum length of about 0.012 mm and a maximum width of about 0.002 mm. (*b*) A material which forms a matrix for the mullite and has a much lower index.

The measured mean index of refraction of this fired clay was found to be 1.582 ± 0.003. By calculation the mean index should be 1.579 if the grains were composed of mullite and cristobalite and 1.565 if the grains were composed of mullite and glass.

Fired at 1,525° C.—The rate of expansion of the clay is again uniform throughout the entire range studied and the total expansion is appreciably lower than that obtained after firing at 1,120° C., which was the lowest of any of the previous measurements. The petrographic examination shows this fired clay to be composed entirely of mullite and a glassy matrix material. The mullite needles are somewhat larger (about 0.004 mm in width) than those found after that firing at 1,400° C. Mean index measurements on grains composed of mullite and the matrix material gave uncertain results. The glassy matrix material was too small in quantity to identify definitely; however, the thermal expansion measurements would indicate that the cristobalite has been wholly converted to glass.

Clay K–1.—*Fired at 1,120° C.*—The petrographic examination showed an amorphous matrix in which are embedded minute particles with a greatly different index and generally high birefringence. The mean index of the grains is about 1.57. The rate of expansion is uniform throughout the entire range measured.

Fired at 1,180° C.—The expansion curve coincides with that obtained after firing the clay at 1,120° C. This would indicate that the formation of mullite from the clay does not occur at as low a temperature as in the case of either clay C–1 or M–1, although there is very little difference in the P. C. E. value of the three clays.

Fired at 1,260° C.—The rate of expansion below 200° C. and the total expansion at both 200° and 900° C. has increased greatly in comparison with that obtained after firing at either 1,120° or 1,180° C. It would appear that the formation of mullite from the clay proceeds at a very rapid rate when once the proper temperature is reached.

Fired at 1,400° C.—The total expansion both at 200° and 900° C. has reached its maximum after firing the clay at this temperature At 200° C. the total expansion is over 260 per cent greater and at 900° C. over 60 per cent greater than that obtained at these temperatures on the specimens fired at 1,120° C. The petrographic examination shows this fired clay to consist of mullite and a matrix material too small in quantity to indentify. An occasional small grain of quartz was observed. The thermal expansion shows that the liberated silica (cristobalite) appeared in greatest quantity during this firing.

Fired at 1,525° C.—The rate of expansion is again uniform throughout the entire range measured and the total expansion is lower than

that obtained on this clay after firing at any of the other temperatures. The inflection in the curve caused by the expansion of the cristobalite has entirely disappeared. The petrographic examination shows the fired clay to consist of small mullite crystals in a matrix material, the index of which it is impossible to determine. The variations which may occur in the thermal expansion of fire clays, depending on the changes in mineralogical composition caused by firing at different temperatures, are shown to unusually good advantage by the data obtained on this clay.

CLAY M–1.—*Fired at 1,120° C.*—The petrographic examination shows that the material is composed largely of an isotropic matrix which has a slightly fibrous texture. Minute inclusions, with an index of refraction very different from the matrix and showing high birefringence, are present. The mean index of the grains is about 1.565. The fibrous texture may be an inheritance from the original platy structure of the clay. The rate of expansion is uniform from 20° to 900° C.

Fired at 1,180° and 1,260° C.—The maximum expansion both at 200° and 900° C. was reached after firing at 1,180° C. and is identical with that obtained after firing the clay at 1,260° C.

Fired at 1,400° C.—The inflection in the expansion curve at 200° C. has entirely disappeared, which is in contrast with clays C–1 and K–1. The petrographic examination shows that the grains are composed only of mullite distributed uniformly throughout a matrix material. Mean index of the grains is about 1.58. The formation of mullite from the clay apparently proceeds at a very rapid rate, and the reaction referred to at the beginning of this section is apparently completed much sooner than in case of either clay C–1 or K–1.

Fired at 1,525° C.—The rate of expansion is uniform and the total expansion is lower than that obtained on the clay after the firings at any other temperature. The petrographic examination shows the grains to be composed only of mullite and a matrix material. The mullite needles are somewhat larger and better developed than in the preceding firing. It is impossible to determine the index of the matrix material accurately, but it appears to be about 1.50. It would appear that the crystalline silica (cristobalite) has been converted to glass.

The data obtained in this study show that these clays have a comparatively straight line expansion when fired at 1,120° C. and are still essentially the same in microscopic appearance as the unfired clay. As the temperature of firing is increased, both the expansion and mineralogical composition change and development of mullite is noted. The petrographic examination of the raw clays showed little or no free quartz present. Therefore, the uncombined silica indicated by the high rate of expansion below 200° C. for specimens fired at certain temperatures above 1,120° C. (example, clay K–1 1,260° C. fire) is believed to have been set free due to the formation of mullite from the clay matter. This excess silica probably forms, according to expansion observations, as cristobalite with possibly some tridymite and gradually changes at increased temperatures to a highly siliceous glass. The petrographic examination shows the mullite needles to be embedded in a glassy matrix which is not present in sufficient quantity to be definitely identified.

The reaction involving the formation of mullite from clay is especially interesting, since it occurs within the range of temperature used in the firing of fire-clay refractories. It is obvious that it may reach varying stages of completion in the refractories placed in different parts of the kiln. It follows, therefore, that the properties of the refractories taken from different parts of a kiln setting must necessarily be different depending on the state of progress of the reaction when arrested.

8. MODULI OF ELASTICITY AND TRANSVERSE STRENGTH

The stress (load) strain (deformation) curves, from which the moduli of elasticity were computed, were determined on specimens approximately 1 inch in cross section and 12 inches long. They were placed across a 10-inch span and loaded at the center.

The transverse strengths (moduli of rupture) of the various fire clays were computed from the loads required to break the specimens on which the load-deflection curves were determined.

The two extreme types of rupture which occurred in the testing of these clay specimens are shown in Figure 9. The upper specimen (1) shows the break to be practically perpendicular to the base of the specimen, and is associated with bodies which are open burning. The specimen (2) just below this shows a type of break which has a tendency to result in a partially curved surface. Such ruptures occur in dense or highly vitrified bodies.

Determinations of moduli of elasticity and rupture were made on specimens of the fire-clay bodies after having been fired at 1,155° C. and also at 1,400° C. Data were obtained at room temperature, 550° and 1,000° C., and the results for the clays fired at the lower temperature are given in Table 5 and those fired at the higher temperature in Table 6. All values, with the exception of those determined at 1,000° C., represent the average of not less than two determinations, either value making up this average varying less than 10 per cent from that average.

Comparing the results obtained at 20° C. on specimens fired at 1,155° C. (Table 5) with those fired at 1,400° C. (Table 6) the following information is obtained:

(*a*) With four exceptions, B–3, C–2, R–2, and R–3, which show decreases, the bodies show greater transverse strengths after the firing at the higher temperature. Although several of the clays show little change, the majority show decided increases ranging to 100 per cent.

(*b*) With two exceptions, B–3 and R–3, the moduli of elasticity of the bodies are greater after firing at 1,400° C. than after firing at 1,155° C. The increases range from a minimum of approximately 5 per cent to a maximum of 120 per cent.

The results obtained in the tests at 550° C. and 1,000° C. are relatively the same as those at 20°.

A comparison of the values obtained at 550° C. with those obtained at 20° C. of specimens fired at either 1,155° or 1,400° C. shows, in general, that the percentage increase in moduli of elasticity and rupture is greater in highly siliceous bodies than in aluminous bodies.

9. PLASTIC FLOW

Deflection readings resulting from the plastic flow measured at 1,000° C. of the 26 fire-clay bodies fired at 1,155° and 1,400° C. are given in Table 8, which is divided into two major parts. The left section presents data obtained on specimens of clay fired at 1,155° C. and the right section those fired at 1,400° C. The first two columns in each section represent the average of increments obtained every five minutes after the first five minutes for one hour when using a stress of approximately 60 lbs./in.^{2} and a second test for a one-half hour period when using a stress of approximately 120 lbs./in.^{2} The load was applied midspan of the 1 by 1 by 12 inch specimens on a 10-inch span.

TABLE 8.—*Plastic flow data measured at 1,000° C. on fire clays*

Clay No.	Clays fired at—					
	1,155° C.			1,400° C.		
	Average deflection readings, taken at 5-minute intervals, on 1 by 1 by 12 inch specimens using a 10-inch span		Total plastic deflection, taken from plastic flow curves, with stress approximately 360 lbs./in.^{2}	Average deflection readings, taken at 5-minute intervals, on 1 by 1 by 12 inch specimens using a 10-inch span		Total plastic deflection, with stress approximately 360 lbs./in.^{2} (taken from plastic flow curves; see footnote No. 14)
	During 1 hour; stress approximately 60 lbs./in.^{2}	During ½ hour; stress approximately 120 lbs./in.^{2}		During 1 hour; stress approximately 60 lbs./in.^{2}	During ½ hour; stress approximately 120 lbs./in.^{2}	
	Inch	*Inch*	*Inch*	*Inch*	*Inch*	*Inch*
A-1	<0.0001	0.0001	0.0025	<0.0001	<0.0001	0.0003
A-2	.0002	.0004	.0048	<.0001	<.0001	.0004
B-1	.0003	.0004	.0063	<.0001	<.0001	.0007
B-2	.0005	.0013	.0208	<.0001	.0001	.0013
B-3	.0053	.0138	.1230	.0005	.0005	.0086
C-1	.0004	.0020	.0156	<.0001	.0001	.0010
C-2	.0007	.0014	.0062	<.0001	.0001	.0008
D-1	.0003	.0004	.0018	<.0001	<.0001	.0003
E-1	.0001	.0002	.0018	.0001		.0003
G-1	.0001	.0002	.0018	<.0001	<.0001	.0005
H-1	.0001	.0003	.0060	<.0001	<.0001	.0004
H-2	.0001	.0001	.0022	.0001	.0001	.0005
H-5	<.0001	.0002	.0020	<.0001	<.0001	.0002
H-6	.0003	.0004	.0050	.0001	.0001	.0004
I-1	.0002	.0003	.0048	<.0001	<.0001	.0002
I-2	.0005	.0011	.0275	<.0001	<.0001	.0005
I-3		.0004	.0030	.0002	.0002	.0025
K-1	.0001	.0003	.0044	<.0001	<.0001	.0010
K-2	.0005	.0006	.0072	<.0001	.0004	.0003
M-1	.0004	.0010	.0184	<.0001	<.0001	.0011
M-2	.0003	.0004	.0056	<.0001	<.0001	.0006
Q-1	.0002	.0008	.0036	<.0001	<.0001	.0007
R-1	<.0001	.0003	.0032	.0001	.0001	.0010
R-2	<.0001	.0002	.0030	<.0001	.0001	.0003
R-3	.0002	.0002	.0036	<.0001	<.0001	.0017
T-1	<.0001	.0002	.0016	<.0001	<.0001	.0004

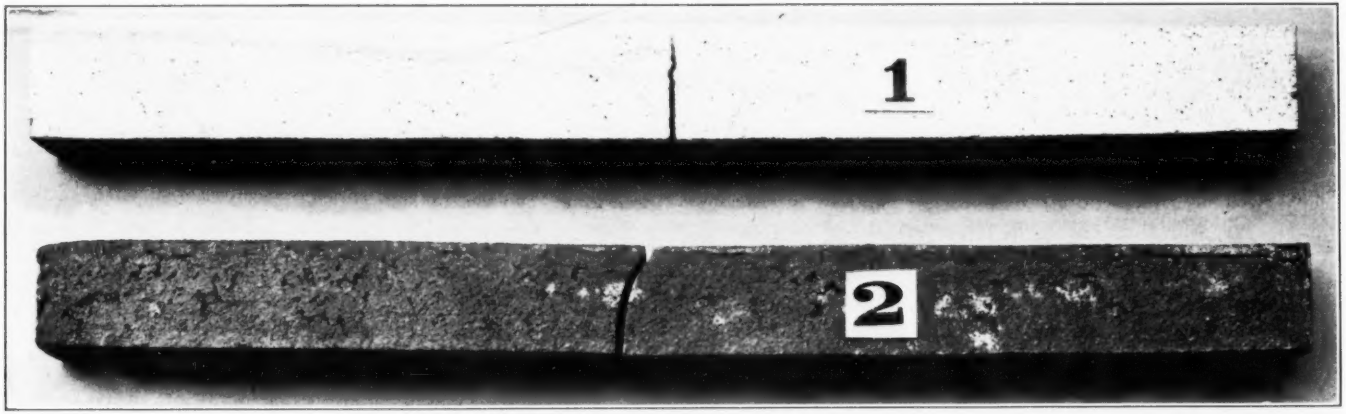


FIGURE 9.—*Showing the two most prevalent types of rupture occurring in specimens of clays tested for modulus of elasticity and rupture*

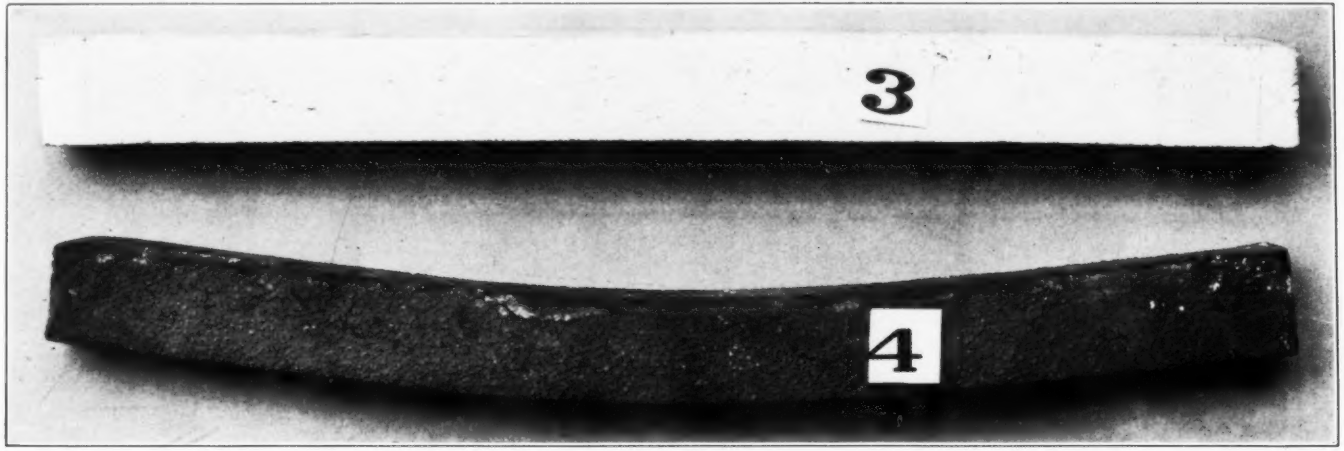


FIGURE 11.—*The lower specimen illustrates a fire clay having a very high plastic flow under load at 1,000° C. Just above this is an untested specimen prepared from clay E–1*

The data obtained with these loads applied to clays B–3 and M–1, which represent two clays of widely different plastic-flow properties, are shown in Figure 10. These curves illustrate the effect of temperature of firing on the plastic flow as well as the relative amounts which take place after the first 5-minute interval. A large part of the deflection taking place during the first-time interval represents the elastic properties of the clay. In the case of clay M–1, fired at

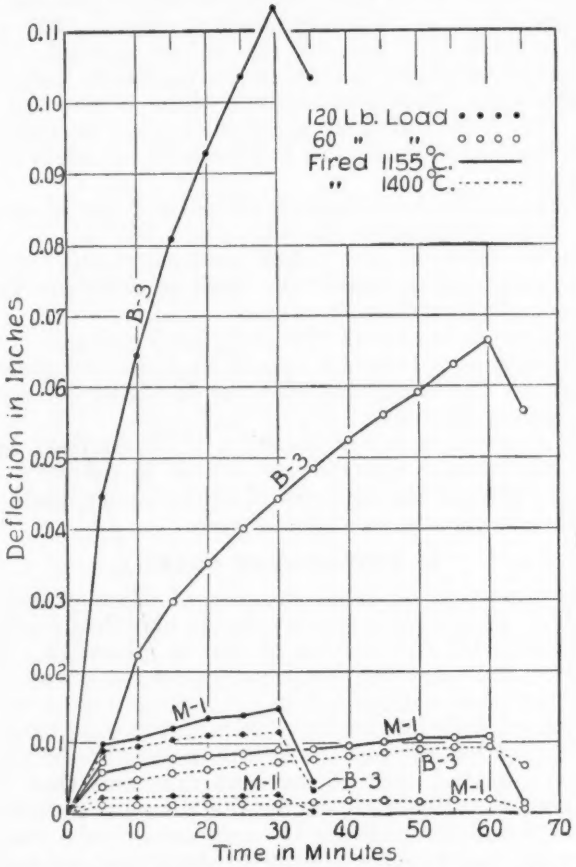


FIGURE 10.—*Time-deflection curves obtained at 1,000° C. on clays B–3 and M–1*

Constant loads of approximately 60 and 120 lbs./in.² were applied for periods of one hour and one-half hour, respectively. As indicated by the curve the final reading was taken after the removal of the load

1,400° C., there is very little plastic flow after the initial time increment. This is in contrast with clay B–3, which shows continued flow to the final reading.

The values given in the third column of each section of Table 8 represent the total plastic deflection in inches of the various clays under a stress of approximately 360 lbs./in.². The values were taken from the plastic-flow curves described as follows in the Progress

Report on Investigation of Fire-Clay Bricks and the Clays Used in Their Preparation: [14]

Typical load-deflection curves as obtained at 1,000° C. on a specimen cut from fire-clay brick are shown in Figure 13. The upper curve shows the plastic flow of the material under these same loads and the middle curve the elastic properties. The elastic recovery of the material was considered as the difference between the total deflection caused by the load and the "set" ("representing plastic flow") of the material on removal of this load. * * *

The results of this study may be summarized as follows:

1. The plastic flow of these clays fired at either 1,155° or 1,400° C. when loads of 60 lbs./in.^{2} and 120 lbs./in.^{2} are applied is very small.

2. The values of plastic deflection are decidedly different for the various clays when loads greater than those referred to under (1) are used. This is indicated by the results given in Table 8 when a load of 360 lbs./in.^{2} is used, and is especially apparent in the clays fired at 1,155° C.

3. The plastic deflections of the clays fired at 1,400° C. are decidedly lower than those of the same clays fired at 1,155° C.

4. The highly siliceous clays [15] show the least plastic deflection after firing either at 1,155° or 1,400° C. Next in order are the siliceous clays, which are followed by aluminous.

5. The plastic deflection of the clays after firing at 1,400° C. is not greatly different. It would appear that the development of the crystal phase in the aluminous clays is decidedly advantageous in decreasing their plastic flow.

Figure 11 shows an untested specimen (3) in contrast with one (4) that has been tested. Specimen 4, which is prepared from clay B–3, deflected beyond the capacity of the testing apparatus without rupturing and represents an extreme case.

10. GROUPING OF CLAYS

With the exception of three samples of silica or quartz (H-3, H–4, and P–1), all are plotted according to chemical analyses on the small section of a triaxial diagram shown in Figure 12. The values given for silica, alumina, and flux are computed to a water-free basis. Since all of the compositions fall in a small section of the diagram, it was considered desirable to show only that section on an enlarged scale. The lower left apex of the section represents 55 per cent alumina, the apex at the right 35 per cent flux, and that at the top 80 per cent silica. The position in the diagram indicated by the cross within the circle represents the composition of a washed North Carolina kaolin, and is given simply to show how the various clays compare in composition to typical kaolin.

The clays have been divided into three groups, as indicated by the dashed lines. The maximum percentage of mullite, which may theoretically be obtained from a clay of given composition fired under favorable conditions for such development, was computed from the chemical analysis (water-free basis). These values are only approximate since, according to the nature of the system, some of the alumina must necessarily have gone into solution with the glass which is present. The line YY' was so placed as to include those clays (Group A) having less than 40 per cent "free silica" after the formation of mullite. The area between lines YY' and ZZ' includes those (Group B) which

[14] B. S. Jour. Research, **3** (RP114). Also J. Am. Ceram. Soc., **12** (10), pp. 640–675; 1929.
[15] Arbitrarily considered as those containing more than 60 per cent silica (water-free basis).

theoretically contain between 40 and 50 per cent "free silica" and those falling above line *ZZ'* (Group C) contain over 50 per cent. Important properties of the three groups are indicated by the values given in the following table:

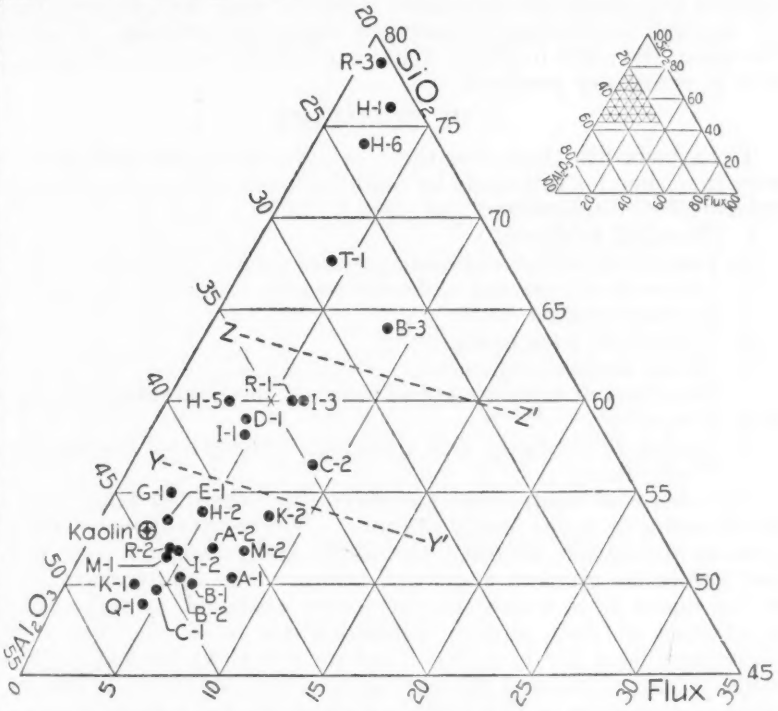


FIGURE 12.—*A section of a triaxial diagram (the shaded portion enlarged of the small triangle on the right) showing the location of clays according to to chemical analysis*

A kaolin is included for comparative purposes only.

These values show the percentage increase in properties for specimens fired at 1,400° C. as compared with those fired at 1,155° C. and are given as average percentages for each group

	Porosity	Modulus of rupture [1] at 20° C.	Modulus of elasticity at 20° C.	Modulus of elasticity at 1,000° C.
Group A (less than 40 per cent [2] free SiO_2)	−10.8	30.8	44.4	133.3
Group B (between 40 and 50 per cent free SiO_2)	−30.6	50.9	71.6	180.7
Group C [3]	−8.8	28.0	37.9	120.3

[1] Determinations for this purpose made on a 4-inch span because of greater number available.
[2] Refers to "free silica" which could theoretically be present after the formation of mullite.
[3] Clay B-3 not considered in group average because of its low P. C. E. value.

These averages indicate that the clays classed in groups A and C have properties which are probably more desirable in clays for the manufacture of refractories than those classed in group B. The percentage change in porosity would indicate that the firing range of clays in group B is shorter than that of the clays included in the other groups. The percentage change in values for moduli of elasticity, both at 20° and 1,000° C., and moduli of rupture show that the percentage of glass in the clays of group B is probably greater or formed

more rapidly at the higher temperature of firing than in groups A and C. However, the average total linear thermal expansion (Table 7) at 1,000° C. of clays in group C is almost 30 per cent greater than that of either of the other two groups. The high expansion of the clays in this group (see expansion curve for clay H–1, fig. 6) is caused by the high percentage of quartz or silica they contain. In general, therefore, the clays in group A have properties which are most desirable in refractory products.

VI. SUMMARY

Twenty-six fire clays and three samples of quartz and silica sand were furnished for this study by manufacturers of fire-clay refractories. Information obtained on these clays included:

1. Chemical analyses.
2. Tempering water and absorption of grog.
3. Linear shrinkage and unfired strength.
4. Porosity of fired clays.
5. Pyrometric cone equivalents.
6. Linear thermal expansion.
7. The effect of temperature of firing on the mineralogical composition of fire clays.
8. Moduli of elasticity and transverse strength of the fired clays.
9. Plastic flow.

The chemical analyses of the clays show them to range from the aluminous type to the highly siliceous. The results of such determinations as absorption, porosity, shrinkage, and pyrometric cone equivalent values are given in a series of tables. The approximate location of the mines from which the clays were obtained, as well as a brief description of their geologic formation are included. The thermal expansions from 20° to 1,000° C. of the fire clays fired at 1,155° and 1,400° C. are given, and the clays are grouped according to the several types of expansion. The moduli of elasticity and transverse breaking strengths have been determined after receiving two different heat treatments, and at several different temperatures.

These data show that the thermal expansions of the fire clays determined after firing at 1,400° C. may be greater or less than after firing them at 1,155 ° C., depending entirely on the composition of the clays. The information given also indicates the successive simultaneous development of cristobalite and mullite, and finally the probable conversion of the cristobalite to a highly siliceous glass.

The moduli of elasticity and rupture of the clays are, with few exceptions, greater after firing at 1,400° C. than after firing at 1,155° C.

Comparing the values for moduli of rupture and elasticity obtained at 550° C. with those obtained at atmospheric temperature show, in general, that the percentage increase in moduli of elasticity and rupture is greater in highly siliceous clays than in aluminous clays. The plastic deflections of the clays, measured at 1,000° C. are much lower for those fired at 1,400° C. than those fired at 1,155° C., and are also lower in the siliceous type of clays than in the aluminous.

The clays are plotted according to chemical composition on a triaxial diagram and are divided into three groups. Those clays which on firing would theoretically contain the greatest percentage of mullite are grouped about a kaolin and have properties which should be very desirable in fire-clay products.

WASHINGTON, February 25, 1930.

A PRECISE AND RAPID METHOD OF MEASURING FREQUENCIES FROM 5 TO 200 CYCLES PER SECOND

By N. P. Case

ABSTRACT

After a brief discussion of some of the common methods of measuring frequencies from 0 to 200 cycles, a method is described which offers important advantages, combining a high degree of accuracy with ease and rapidity of use. The method depends on the fact that if a condenser be discharged through a resistance n times per second (the condenser being charged to the same initial voltage each time), then the average voltage drop across the discharging resistance is directly proportional to n. The unknown frequency is made to control the number of times per second the condenser is discharged, and thus the voltage drop mentioned above is proportional to the unknown frequency. A circuit arrangement is described whereby this voltage drop is balanced through a sensitive galvanometer and high resistance, against a known fraction of the total voltage drop along a slide-wire resistance shunted around a storage cell. By first calibrating the system with an alternating current of known frequency, it is possible to read unknown frequencies directly off the slide wire.

A discussion of the sources of error and experimental determinations of the error actually observed, lead to the conclusion that, in the range from 5 to 200 cycles per second, the accuracy is always better than one-tenth cycle.

CONTENTS

	Page
I. Introduction	237
II. Early work	238
III. Final design	239
IV. Theory	240
V. Method of operation	241
VI. Accuracy obtainable	242

I. INTRODUCTION

During the course of the work carried on by the Bureau of Standards in the development of secondary standards of frequency, it is necessary to make daily measurements of the beat frequencies between various piezo oscillators used as secondary standards. As some of these secondary standard piezo oscillators do not vary in frequency from day to day by more than a few tenths of a cycle per second, the method of measuring the beat frequencies should be accurate to better than a tenth of a cycle per second. The frequency range of the beat notes to be measured is usually from 0 to about 100 cycles per second.

One method of measurement used is to record the beat frequency photographically on an oscillograph, at the same time impressing second signals on the record from a standard clock. As the constancy of the piezo oscillators improved, however, it became apparent that this method required too much time to be practicable. In order to obtain an accurate record by this means, it is necessary to let each

exposure run for about 20 seconds. This gives a record which is very arduous to count, and the number of measurements to be made is such that the complete process of intercomparing all the piezo oscillators and reducing the results occupies too much time.

II. EARLY WORK

Consideration was given to the possibility of using a direct-reading frequency bridge, special consideration being given to the modified form of Hay's bridge, as described by Soucy and Bayly.[1] This arrangement was not found to be entirely suitable for the purpose, however, for two reasons: (1) In order to secure adequate sensitivity in the region of very low frequencies used, it would be necessary to use an unreasonably large air-core inductance, and (2) as an aural balance would not be sufficiently accurate, because of the low sensitivity of the ear at these frequencies, it would be necessary to use a tuned vibration galvanometer, which is not considered practicable in view of the wide range over which it would have to be tuned.

The arrangement presented in this paper is an outgrowth of a system originally described by Maxwell[2] for rough measurements of capacity. Figure 1 is a circuit diagram of the arrangement as altered by Fleming and Clinton.[3] The alternating current, the frequency of which is to be determined, is fed into a polarized relay at *A*. On one-half of each cycle the contactor is drawn to contact *1*, charging the condenser to the voltage of the battery. On the other half of each cycle, the contactor moves to contact *2*, discharging the condenser through the milliammeter. Obviously, as long as the time constants of the circuits are kept low enough so that charge and discharge are complete within the limits of error of the measurement, the quantity of electricity which passes through the milliammeter in a given time interval depends solely on the number of times the condenser is discharged in that interval, and, hence, on the frequency of the alternating current applied to the polarized relay. Therefore, the reading of the milliammeter is directly proportional to the frequency. In practice, of course, the instrument has to be calibrated by applying a known frequency, say, 100 cycles per second, to the polarized relay, and then adjusting the battery voltage and the capacity until the meter reads 100. Then if some other frequency is applied to the relay, the milliammeter reading will give the frequency directly. The accuracy, however, is only of the order of 1 per cent of the full-scale reading of the milliammeter, which, while sufficient for many laboratory purposes, was not great enough for the measurements required.

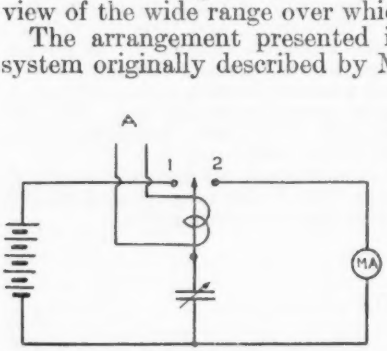


FIGURE 1.—*Circuit arrangement for measuring frequency by means of deflection discharge of a condenser through a milliammeter*

[1] Soucy and Bayly, A Direct Reading Frequency Bridge for the Audio Range, Based on Hay's Bridge Circuit, Proc. I. R. E., 17, p. 834; May, 1929.
[2] Maxwell, Electricity and Magnetism, sec. 775, vol. II.
[3] Fleming and Clinton, On the Measurement of Small Capacities and Inductances, Proc. Phys. Soc London, 18, p. 386. See also F. A. Laws, Electrical Measurements, p. 373; 1917.

III. FINAL DESIGN

It was recognized that the sensitivity of the above arrangement could be made amply sufficient by converting it to a null method and using a sentitive galvanometer. It was desirable also to have the readings directly in frequency. The circuit arrangement finally used is shown in Figure 2. The voltage divider S is a slide-wire, with a thousand divisions on the scale, and accurate to the nearest quarter division at any point on the scale. The voltage is measured across the resistance R, through which the condenser C discharges. The resistance r is inserted to serve a double purpose; to keep the galvanometer from being greatly overdamped, since R and S are both of low resistance; and, more important, to limit the current that is drawn from the slide-wire. At first sight this appears to be an anomalous condition, since the adjustment is made to give zero reading on the galvanometer, but it must be remembered that a continuous voltage is being balanced against the average value of a pulsating voltage. This pulsating voltage is relatively very high during a very short part of the pulsation period, and is practically zero for most of the period. Therefore, there is only one instant during each pulsation when the galvanometer current is actually zero.

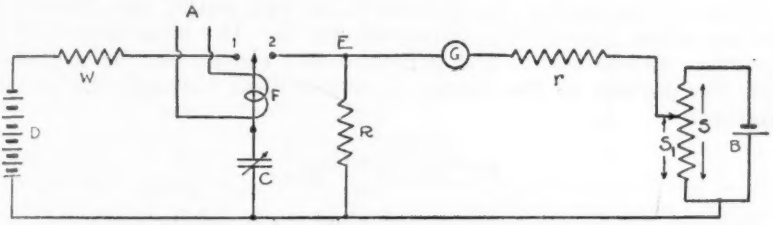


FIGURE 2.—*Schematic diagram of circuit arrangement used for measuring low frequencies*

The galvanometer current is limited to a small value, since the resistance r (fig. 2) must be large for the settings of S_1 to be correct. In order that a small variation in S_1 may give an appreciable deflection, a high-sensitivity galvanometer must be used. As the accuracy of calibration of the slidewire is about 2½ parts in 10,000, the resistance r should be of such a value that the resistance of S is not greater than 0.00025 of r. As S is 7½ ohms, it follows that r should be at least 30,000 ohms. A resistance of 50,000 ohms was used, as that size happened to be available, and the galvanometer was of ample sensitivity. A damping shunt was affixed to the galvanometer and adjusted so that the instrument was not quite critically damped.

The resistance R is low enough in comparison with r so that the variations in the voltage of the point E, as the slider is moved from one end of S to the other (the relay being open circuited), are negligible compared to the voltage of the battery D. If this condition is not fulfilled, the condenser will discharge to varying voltages, depending on the setting of S, and the reading of the latter will not be linear with the frequency of the discharge. A resistance of about 100 ohms was used for R, and a capacity of about 2 μf for C. Both are adjustable in small steps, although it would be sufficient if either one were so adjustable, in order to get a balance for the initial setting. The

resistance W is inserted to limit the initial charging current, and is not critical in value.

Values of circuit constants as used by the Bureau of Standards are as follows:

$D=90$ volts	$r=50{,}000$ ohms.
$W=100$ ohms.	$S=7.5$ ohms.
$C=2.111$ μf.	$B=2$ volts.
$R=100$ ohms.	

The galvanometer has a sensitivity of about 10,000 megohms, and a resistance of about 600 ohms.

IV. THEORY

If the circuit conditions noted above, namely, R and S small compared to r, are complied with, the approximate theory becomes very simple. Referring to Figure 2 the moving contact of the relay F is closed in position *1* and *2*, respectively, for sufficient time so that complete charge and discharge of condenser C is obtained. The charge q on C is

$$q=Ce \tag{1}$$

where e is the voltage of battery D.

When C discharges, the current takes two paths, one through R and the other through the galvanometer G. If r is so large that all the other resistances in the galvanometer circuit can be neglected, then the portion of the charge q_g which flows through the galvanometer is

$$q_g=q\frac{R}{R+r}=Ce\frac{R}{R+r} \tag{2}$$

If there are f discharges per second, then the quantity per second is

$$fq_g=fCe\,\frac{R}{R+r} \tag{3}$$

The steady current through the galvanometer from the battery B, assuming r large with respect to S, is

$$i_g=\frac{S_1}{S}\,\frac{E}{R+r} \tag{4}$$

where E is the voltage of the battery B. The adjustment is made such that the effect of the current i_g on the galvanometer is equal and opposite to the integrated effect of the pulsating current fq_g. Therefore, equating equations (3) and (4)

$$fCe\,\frac{R}{R+r}=\frac{S_1}{S}\,\frac{E}{R+r} \tag{5}$$

$$f=\frac{S_1}{S}\,\frac{E}{eCR} \tag{6}$$

However, it is possible that the galvanometer may not integrate the pulses of current from the condenser properly, and, hence, may not read zero, even though equation (5) is satisfied. This condition is brought about by either of two causes: (1) The magnetic field at the

galvanometer coil may not be constant, and (2) the coil itself may contain magnetic impurities.[4]

An experimental method used by Curtis and Moon to determine whether or not a given galvanometer integrates correctly is illustrated by the circuit of Figure 3. Care should be used with this arrangement in order to avoid damaging the galvanometer, especially if it is one of high sensitivity. The voltage of the battery should be small, the capacity of the condenser likewise small, and the resistances should be high enough to limit the initial currents on charge and discharge to safe values. If the galvanometer reads zero in the arrangement of Figure 3, it may be safely assumed that it will integrate correctly in the frequency measuring network.

V. METHOD OF OPERATION

A tube-driven elinvar tuning fork was available for calibrating the slide-wire. The fork frequency was 99.98 cycles per second, remaining constant at all times to within 1 part in 10,000.

The method of operation is extremely simple. The tuning fork output is applied at A (fig. 2) and the slider on S set so that the scale reading is 999_8 (the last figure being beyond the calibration, must be estimated). Then the capacity of the condenser, the resistance R, or both, are varied until the galvanometer reads zero. If, now, the alternating current, the frequency of which is to be measured, is applied at A, the slider of S is moved until the galvanometer again reads zero, all the other circuit constants remaining invariant. The frequency desired can then be read directly from the scale of the slide-wire. For instance, if the setting is 724_9, the frequency is 72.4_9 cycles per second.

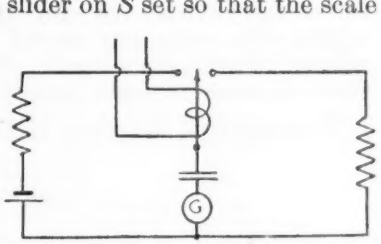


FIGURE 3.—*Circuit arrangement used to determine suitability of galvanometer*

If measurements of high precision are desired, it is advisable to redetermine the setting for the standard frequency before each series of measurements. This is necessary because of changes in battery voltages, and the changes in resistance and capacity of the circuit elements due to temperature changes. The battery circuits should be closed for a sufficient length of time before measurements are made so that the batteries and resistances can come to a condition of equilibrium.

For frequencies below five cycles per second the individual impulses to the galvanometer become objectionable and the balance point can not be accurately located. However, such low frequencies can be determined readily by merely counting the swings of the needle of the milliammeter (which is in the plate circuit of the last tube of the beat note amplifier) over a short period of time. A stop watch can be conveniently used.

In order to extend the range to higher frequencies it is only necessary to set the point for calibration at some lower point of the slide-wire and multiply the scale accordingly. For example, under the condi-

[4] For a full discussion of this effect, see Curtis and Moon, Absolute Measurement of Capacitance by Maxwell's Method, B. S. Sci. Paper No. 564, p. 507, ff.

tions given above, if instead of using 99.98 for the first setting, 49.99 is used, then 99.98 will represent 200 cycles per second. The limitation is, of course, in the frequency to which the relay will respond. The limitation of the relay used is about 200 cycles per second.

VI. ACCURACY OBTAINABLE

Although the slide-wire is only claimed to be accurate to a quarter of a division, corresponding to 0.025 cycle per second, settings on a given frequency will usually repeat to 0.01 cycle per second.

The linearity of the scale has been verified in two distinct ways. (1) A constant-speed alternator with 100-cycle and 10-cycle rotors on the same shaft, assuring that the one frequency is exactly one-tenth of the other, was available. The slide was balanced at 100 cycles per second, and then the 10-cycle frequency was measured in the regular manner, the scale reading obtained was 10.02 ± 0.005 (estimated) cycles per second. This error is less than the error of calibration of the slide-wire. (2) Numerous checks were also made at various odd frequencies, reading the frequency on the slide, and recording it on the oscillograph at the same time. These checks consistently agree within 0.03 cycle per second. Hence the maximum error is well within 0.1 cycle per second. No checks were made above 100 cycles, since all measurements desired were below this value.

WASHINGTON, March 8, 1930.

COEFFICIENT OF FRICTION OF FABRICS

By Alfred A. Mercier [1]

ABSTRACT

This paper describes a simple method for specifying the slipperiness of fabrics, by measurement of the coefficient of friction between two pieces of the same material. A block covered with a sample of the fabric to be tested is placed on an inclined plane which is covered with another piece of the same fabric. The angle between the inclined plane and the horizontal is then increased to a value at which the block just begins to slide. Owing to a rearrangement of the fibers in the surfaces of the fabric this minimum angle decreases with successive slides. A number of slides are, therefore, made until a constant limiting angle is found. The tangent of this limiting angle is defined as the coefficient of friction for the fabric. Some applications of this measurement are mentioned, and illustrative results are given.

CONTENTS

		Page
I.	Introduction	243
II.	Coefficient of friction	244
III.	Apparatus	244
IV.	Test procedure	245
V.	Illustrative results	246

I. INTRODUCTION

The utility of fabrics for certain purposes depends to a large degree on their surface characteristics. For example, slipperiness is undesirable in the backing of rugs but is required of linings used in coat sleeves, shoes, and jewelry cases, and is a prominent feature of sleeping garments. The "creeping" of garments over one another, particularly the creeping of some underwear, is an objectionable feature which is related to the slipperiness or smoothness of the surface.

The surface characteristics vary with (*a*) the material (cotton, wool, silk, or rayon), (*b*) the construction of the yarn (hard or soft), (*c*) the weave (square, twill, or fancy), and (*d*) the finish. A smooth surface is more slippery than a napped surface. The creeping of a garment is noticeable when the fabric of which it is made is nearly of the same weight, but of different surface texture from the fabric with which it is in contact. The lighter of the two fabrics will creep up on the heavier one unless the former has a more slippery surface. Wool garments do not tend to creep because their weight is usually greater than the weight of the adjacent undergarment.

The present paper describes a simple method for specifying the slipperiness or smoothness of a fabric in terms of the coefficient of static friction between two pieces of the same material. The work was done in connection with the fine fabric investigations of the Cotton-Textile Institute and the Bureau of Standards.

[1] Research associate of the Cotton-Textile Institute (Inc.) at the Bureau of Standards.

II. COEFFICIENT OF FRICTION

When a rectangular block is placed on an inclined plane, as in Figure 1, its tendency to slip under the pull of gravity is opposed by the friction between its lower surface and the surface of the plane. The weight of the block (W) exerts a force (N) normal to the inclined plane and a force (F) parallel to this plane. The frictional force (F') resists the slipping tendency due to (F). If the angle between the inclined and horizontal planes is increased (F) becomes greater and (N) smaller. Until (F) exceeds a certain value the block will not slide. When the value of the angle (a) is such that the force (F) equals the frictional force (F') slipping is impending and the ratio of the limiting frictional force (F') to the normal force (N') is called the coefficient of static friction between the block and the plane. From the geometry of the figure this ratio can be shown

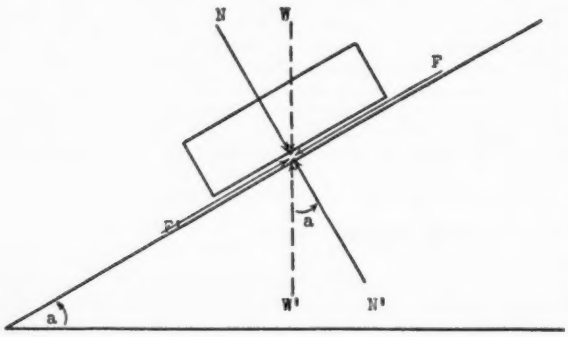


FIGURE 1.—*Diagram of forces on inclined plane*

to be the tangent of the angle (a). Thus

$$F' = W' \sin a$$
$$N' = W' \cos a$$

and

$$\text{coefficient of friction} = f = \frac{F'}{N'} = \frac{W' \sin a}{W' \cos a} = \tan a$$

The result obtained when the block and the inclined plane are both covered with the same fabric is the coefficient of friction for this fabric on itself.

The coefficient of friction is independent of the area of the surfaces in contact, and is also independent of the weight of the block providing the pressure of one surface on the other does not modify the original surface characteristics of the fabric. The coefficient of friction depends on the smoothness of the surfaces in contact and on the presence of a lubricant, such as oil or other finishing material between the surfaces.

III. APPARATUS

A photograph of the apparatus is shown in Figure 2. Two boards each 22 inches long and 6 inches wide, are hinged together at one end. One of the boards rests on three small supports which can be adjusted to bring the board to a horizontal position. The angle between the boards can be changed by a screw arrangement, and this angle or its tangent read on a scale on the upper surface of the horizontal board. The block of wood, 8 inches long and 6 inches wide, weighs about 1¼ pounds. This block and the inclined plane are covered with the fabric to be tested. Clamps for holding the fabric on the block and on

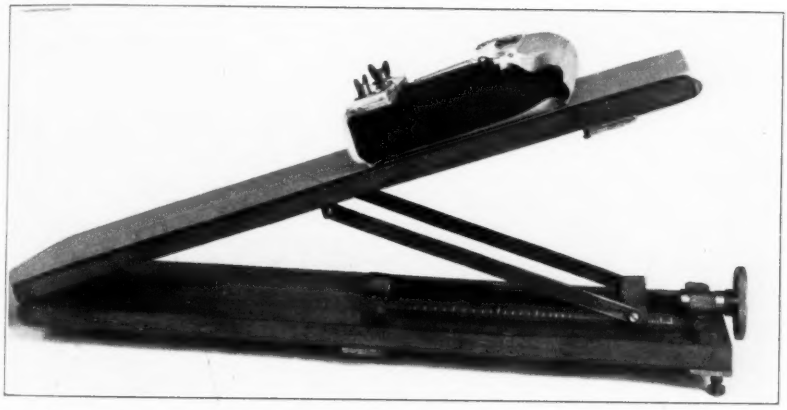


FIGURE 2.—*Device for measuring coefficient of friction between fabrics*

the inclined plane are shown in the figure. A spring keeps the fabric under tension on the block and a small weight clamped to the lower end of the fabric keeps the fabric taut on the inclined plane during the test.

IV. TEST PROCEDURE

The covered block is placed on the inclined plane and the plane is raised to a point where, with the assistance of light tappings on the board, the block begins to slide. The sliding angle is noted and the plane is lowered several degrees. The block is again placed on the inclined plane and the above procedure then repeated several times. For some fabrics the angle between the planes, for the first few slides will decrease one or more degrees with each slide because of a rearrangement of the fibers. As the surface gradually approaches a constant condition, the angle of inclination approaches a constant value. The tangent of this limiting angle is taken as the coefficient of friction for the particular fabric under test.

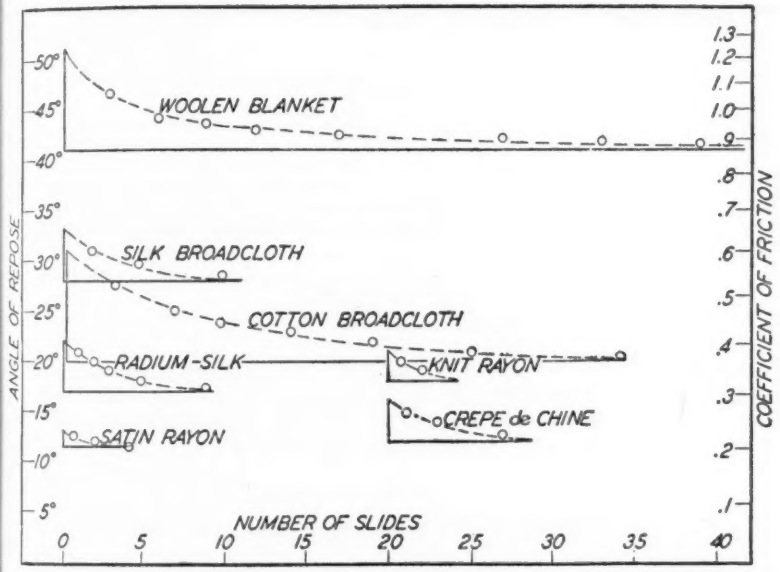


FIGURE 3.—*Angles of repose and coefficient of static friction after successive slidings of fabric on fabric*

The decrease in the coefficient of friction, from its initial value for the first slide to its final value for the limiting angle, may be taken as an indication of the texture of the fabric. This is illustrated by fabrics whose fibers have a tendency to extend above the surface. Thus fabrics with short fibers and napped surfaces show greater changes in the coefficient of friction than fabrics with a smooth finish. The coefficient of friction for a fabric with a smooth surface is less than that for a fabric with a napped surface.

V. ILLUSTRATIVE RESULTS

The results of tests on a variety of fabrics are shown in Figure 3. Angles between the two planes may be read at the left of the diagram and the coefficient of friction at the right. In every case the slide was made in the warp direction of both specimens. The results shown are for fabrics of different materials and weaves so that the position of each material on the diagram does not indicate the position that would be occupied by another fabric made from the same material but of different weave. The results show that variations in the coefficient of friction of fabrics can be recorded with the apparatus herein described. The results also indicate that a complete study of the slipperiness of fabrics would include the effect of weaves, yarns, and finishes for each material.

WASHINGTON, February 24, 1930.

ACCELERATED TESTS OF ASPHALTS

By O. G. Strieter[1]

ABSTRACT

Equipment and methods for testing asphalt by accelerated weathering are described.

A variety of asphalts are shown to exhibit the same type of changes when exposed alternately to a cycle consisting of light from an inclosed carbon arc, water spray, and sudden temperature changes as when exposed outdoors under actual weather conditions.

CONTENTS

	Page
I. Introduction	247
II. The accelerated weathering cycle	247
III. Method of preparing test panels	248
IV. Outdoor exposures versus accelerated tests	248
V. Experiments and results of accelerated weathering tests on asphalts	250
1. Value of tests	250
VI. Summary	253

I. INTRODUCTION

This paper describes the equipment and methods developed at the National Bureau of Standards for accelerated weathering tests of asphalts; discusses the results obtained by its use; and suggests applications of this method in the solution of problems encountered in asphalt technology.

II. THE ACCELERATED WEATHERING CYCLE

The purpose of the accelerated weathering test is to produce rapid changes in the asphalt under conditions simulating outdoor exposure.

The equipment is essentially the same as that of Walker and Hickson,[2] consisting of three carbon arc lamps operating at 220 volts d. c. and 13 amperes. Each lamp is equipped with a cylinder with 3-inch slots for holding the test specimens or panels and each cylinder is geared to a driving mechanism which rotates it once in 20 minutes. Light spray simulating gentle rain is obtained from vertical water jets which may be operated in conjunction with the lights. Lawn sprinklers, with rotating arms, are used for vigorous spraying.

The heat produced by the lamp maintains a temperature of approximately 140° F. at the surface of the panels. A refrigerator, as a separate unit, is used to obtain sudden temperature changes.

Figure 1 gives a photographic view of the accelerated weathering equipment.

[1] Research associate, Asphalt Shingle and Roofing Institute.
[2] Accelerated Tests of Organic Protective Coatings, B. S. Jour. Research, **1**, p. 1; July, 1928.

The daily accelerated weathering cycle is as follows:

18 hours light (overnight).
1 hour refrigeration at −10° F.; three times per week.
3 hours rain (lawn sprinklers).

This cycle admits of numerous modifications to produce more frequent changes in the weathering conditions. However, in this work only the simplest cycle was used since, in general, more frequent changes do not affect the ultimate result, but merely hasten the test.

After the conclusion of the experiments described in this paper the cycle was modified as follows:

Cold, 1¾ hours, 8.45 a. m. to 10.30 a. m.
Rain, 1 hour, 10.45 a. m. to 11.45 a. m.
Light, 1½ hours, 12 m. to 1.30 p. m.
Rain, 2 hours, 1.45 p. m. to 3.45 p. m.
Light, 16½ hours, 4 p. m. to 8.30 a. m.

This cycle gives quicker results and is recommended as a tentative standard of test.

III. METHOD OF PREPARING TEST PANELS

For consistent results asphalt coatings of uniform thickness are essential. The following apparatus has given satisfactory results.

A brass pipe, 12 inches long and 1.5 inches in diameter, is mounted above a block of wood (2 by 4 by 12 inches); the frame being constructed to permit raising or lowering the pipe. An electric heating coil inside the pipe, controlled by a rheostat, heats the pipe to the desired temperature.

The asphalt is melted at the lowest possible temperature and poured on an aluminum panel and allowed to cool. The pipe is adjusted to give the thickness of coating desired and the panel is slowly passed back and forth between the pipe and block several times. If the panel is placed on several sheets of strong typewriter paper, folded once lengthwise, the upper layer of paper can be used to pull the panel back and forth and the lower paper will protect the block of wood from any excess asphalt. Care must be taken to keep the pipe clean. All coatings described in this paper were 0.025 ± 0.003 inch in thickness. Aluminum was used in these tests as a more suitable material for panels than glass, wood, or iron, because of freedom from breakage and relative freedom from moisture or air. Asphalt adheres very well to aluminum.

Panels for the tests in this paper were prepared by the simple device described above. An improved model of a coating machine for which the author is indebted to L. Kirschbraun, of the Flintkote Co., is shown in Figure 2. This improved model will be used in future tests.

IV. OUTDOOR EXPOSURES VERUS ACCELERATED TESTS

Preliminary outdoor exposures, to check results of accelerated tests, were made in Petri dishes, as this method of exposure is largely standardized in asphalt testing. Later the outdoor exposures were made on aluminum, prepared as for the accelerated tests.

The presence of cracks, extending through the coating to the metal, as evidenced by visual inspection, was taken as the end point

B. S. Journal of Research, RP197

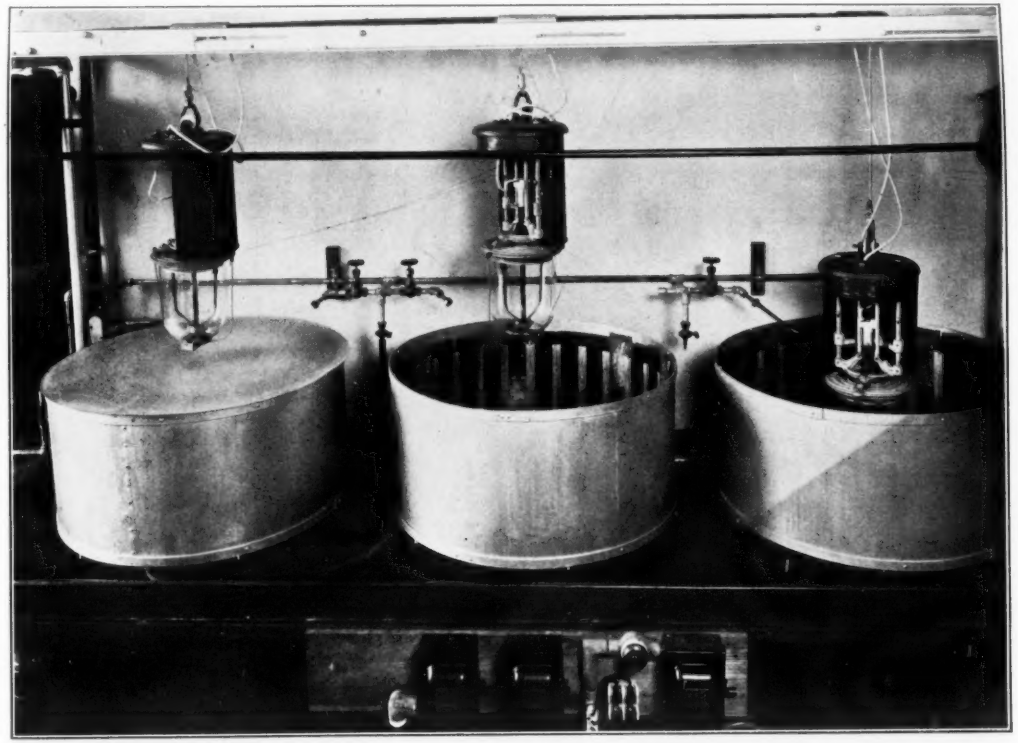


FIGURE 1.—*The accelerated weathering tester*

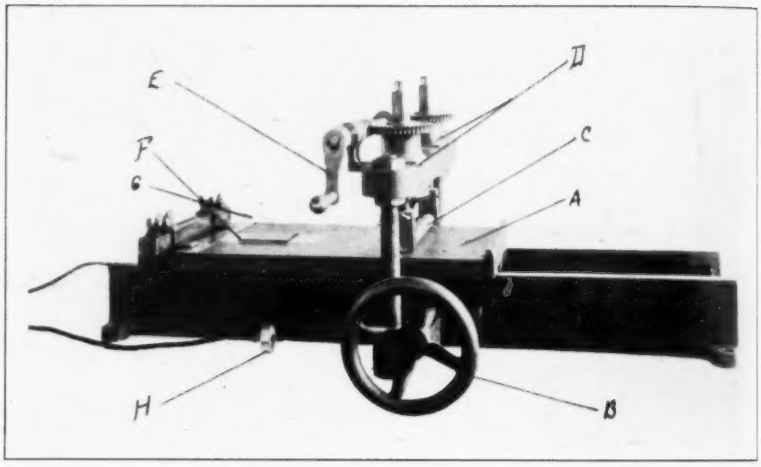


FIGURE 2.—*Coating machine with panel in position for coating*

A, Bed plate; *B*, hand wheel for moving bed plate; *C*, doctor, or heating tube (electrically heated); *D*, micrometer screws (graduated in 0.001 inch divisions); *E*, crank for turning micrometer screw and adjusting doctor; *F*, panel in position for coating, *G*, brass strip; *H*, plug and cord for heating element.

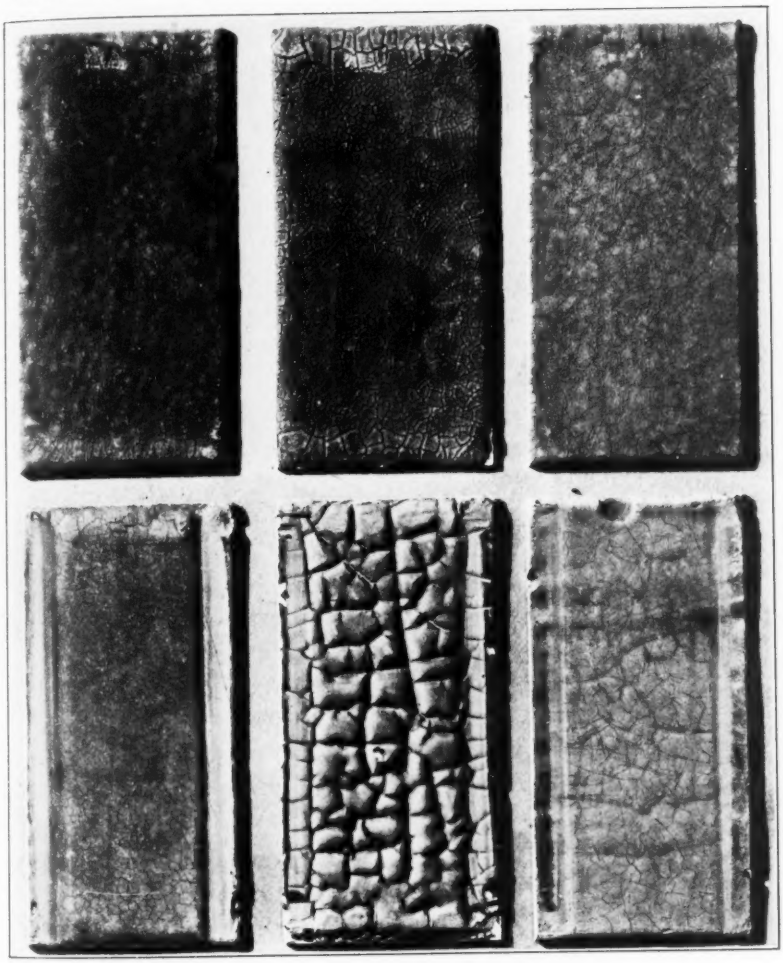


FIGURE 3.—*Outdoor versus accelerated exposure*

The panels shown in upper row were exposed outdoors to actual weather conditions for 1½ years. The panels immediately below these are their duplicates and were exposed in the accelerated test for 70 days.

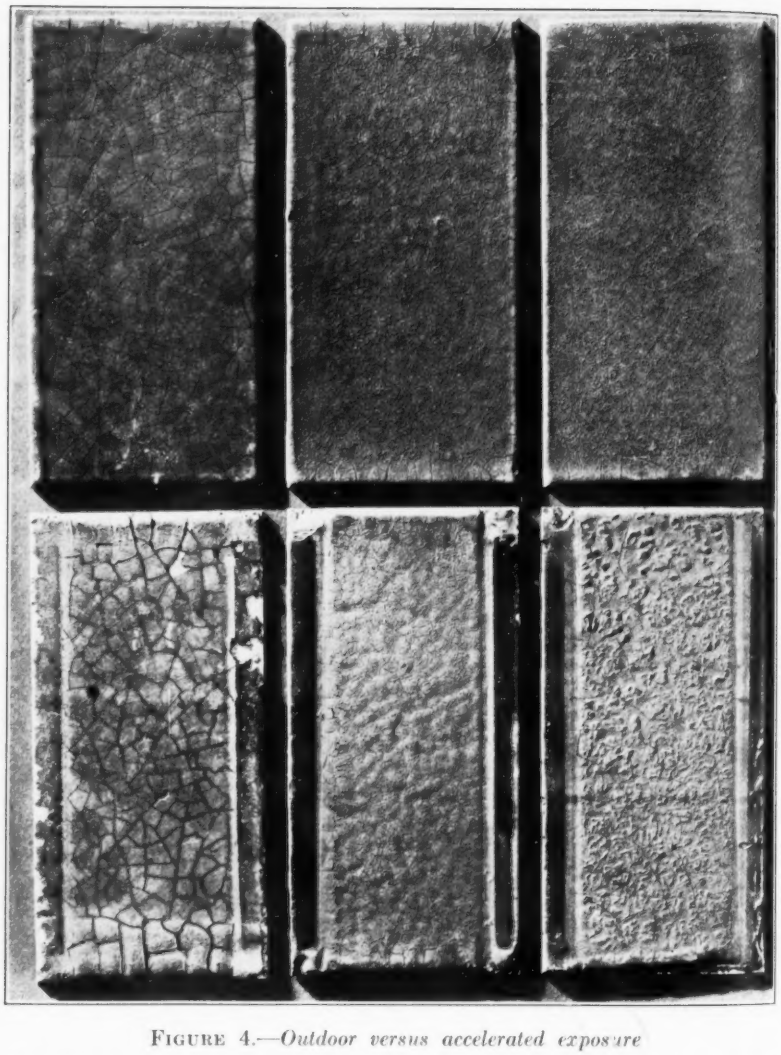


FIGURE 4.—*Outdoor versus accelerated exposure*

The panels shown in upper row were exposed outdoors to actual weather conditions for 1½ years. The panels immediately below these are their duplicates and were exposed in the accelerated test for 70 days.

of the test. In all cases the changes on outdoor exposure occurred in the same order as in the accelerated test, showing that the accelerated test is a true measure of the relative durability of asphalts.

In Figures 3, 4, and 5 the panels are especially grouped to bring out the relation between outdoor and accelerated weathering. The melting points of these asphalts were around 220° F. The panels were prepared by the method previously described by pouring the melted asphalt on slightly preheated aluminum sheet metal (3 by 6 by one-sixteenth inch) and then passing, after cooling, under the heated pipe until the desired thickness of 0.025 inch was obtained.

The panels shown in the upper rows of the photographs were exposed outdoors for one and one-half years. The asphalt samples exposed to the accelerated cycle are shown in the lower rows. These were exposed to the cycle for 70 days. An examination will show great similarity in appearance of these panels, particularly in the nature of their behavior as checking, cracking, flatness, and contraction.

In Figure 3 the first panel in the upper row shows similarity with its duplicate immediately below in its flatness and in the nature of its checks, which tend to form an irregular network. The word "flatness" refers to a peculiar smoothness of these panels. The center panels do not show flatness, but show a similar network of checks. The checking is more pronounced in the lower panel (accelerated test), but the type of change is the same. This sample was specially prepared to obtain an asphalt of poor weather-resisting qualities. The third panel (upper row) shows checking and straight cracking. The accelerated test (lower row) shows the same results as the outdoor exposure, only that the accelerated panel shows more flatness. The development of a "flat" and matt appearance is characteristic of paraffin-base asphalts.

In Figure 4 all the panels show flatness, most pronounced in the first and least in the center panels. The results obtained are similar in the accelerated and outdoor exposures. In the third set there are slight protuberances on the accelerated panel which do not show in the outdoor exposure. Refrigeration when used daily greatly retarded the formation of such protuberances, both as to size and number.

Figure 5 shows some new effects, more pronounced in the accelerated tests than in the outdoor exposures. In the third set of panels the checking is similar, as may more easily be detected by means of a magnifying glass. In the center set of panels grooving is shown, irregular in the outdoor panel and deep lines in the accelerated panel. The first set of panels show hummocks in addition to grooving, a mild form in the outdoor exposure and exaggerated in the accelerated exposure.

These examples have been given to show the remarkable similarity in the nature of the changes of asphalts under the two conditions of exposure. No attempt has been made to establish an exact ratio between outdoor exposure and the accelerated cycle.

V. EXPERIMENTS AND RESULTS OF ACCELERATED WEATHERING TESTS ON ASPHALTS

1. VALUE OF TESTS

The accelerated weathering cycle is valuable, not only because it produces in a short time results which are similar to long-time exposures outdoors, but also because it readily produces results which are useful in identifying kinds or types of asphalt and furnishes a method for detecting differences in the composition of asphalts. As Figures 3, 4, and 5 show, such types and differences of asphalts may also be detected upon outdoor exposure. The results, however, are not as distinct and the tests require much more time.

The results from the accelerated weathering tests may be described qualitatively and quantitatively.

The qualitative result is obtained in from 1 to 10 cycles of exposure to the accelerated cycle and is useful in determining the type of asphalt as evidenced by its characteristic behavior.

Asphalts may be grouped into types according to their characteristic behavior in the accelerated weathering cycle. In general, from four to six types should be distinguished for a complete study. For the sake of simplicity, however, only two types will be considered here, namely, type A and type B.

Type A.—These asphalts check when exposed to the accelerated cycle. They remain glossy for a relatively long time. After prolonged exposure to the cycle, the checks extend through the coating to the surface of the aluminum panel. Figure 6 illustrates this type of asphalt. This panel was exposed for 70 days to the accelerated cycle. The irregular form of the checks and their rounded edges (checking) are characteristic of this type of asphalt.

Type B.—These asphalts do not check. After 18 hours of exposure to light they become dull and show a flat, smooth, and streaked surface. When sprayed with water the asphalt takes on a grayish-green surface film. After prolonged exposure the asphalt cracks through to the surface of the aluminum. These cracks form long straight lines and run in every direction over the surface of the panel (cracking). This type of behavior is well shown in the first set of panels of Figure 4. This type is further illustrated by Figure 7. The asphalts in this group (fig. 7) were made from various kinds of crudes, but all came from the same petroleum fields. Their physical constants are shown in Table 1:

TABLE 1.—*Physical constants of asphalts*

Plate No.	Material	Softening point	Penetration	Ductility	Characteristic behavior to accelerated weathering	Remarks
		°F.				
100	Type B asphalt	223	25	1.4	Type B	These asphalts were made from various semiasphaltic crudes.
102	do	272	22	1.4	do	
106	do	230	25	1.8	do	
138	do	222	17	2.0	do	

When different asphalts are refined in the same manner it is frequently possible to determine their origin by exposure to the accelerated cycle and noting the characteristic behavior. However,

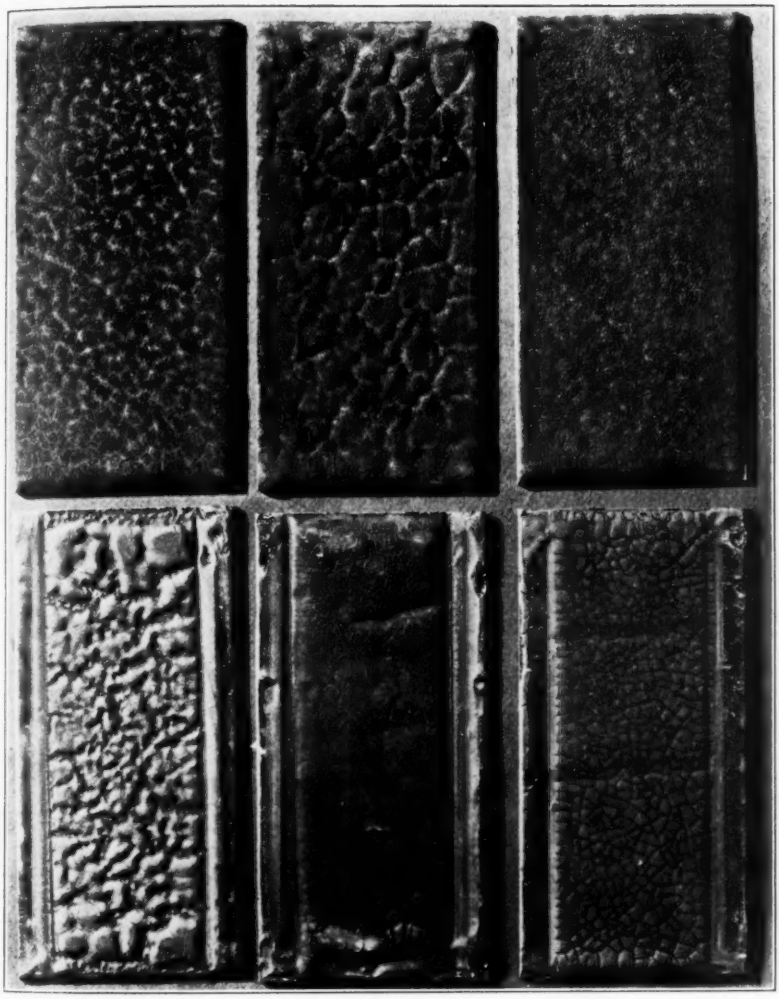


FIGURE 5.—*Outdoor versus accelerated exposure*

The panels shown in upper row were exposed outdoors to actual weather conditions for 1½ years. The panels immediately below these are their duplicates and were exposed in the accelerated test for 70 days.

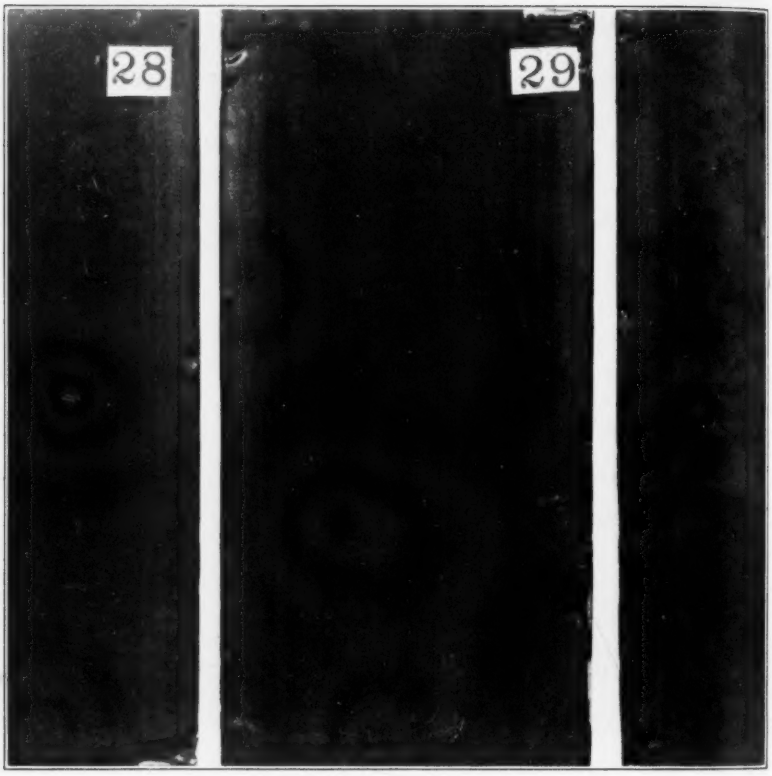


FIGURE 6.—*Accelerated exposure, type A asphalt*

The check formation is characteristic for this type of asphalt.

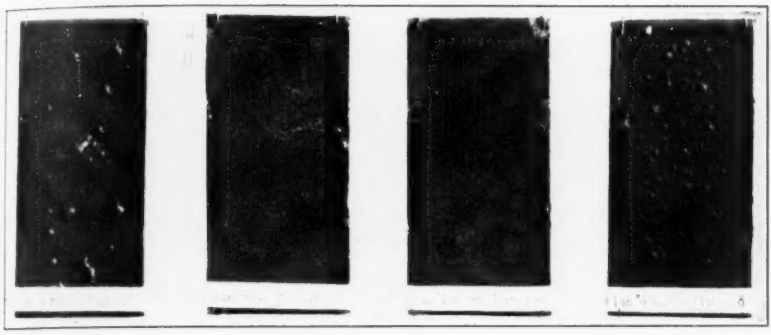


FIGURE 7.—*Accelerated exposure, type B asphalts*

The asphalts in this group were made from various kinds of crudes, but all came from the same petroleum fields. Their behavior is similar on exposure to the accelerated cycle. (See Table 1.)

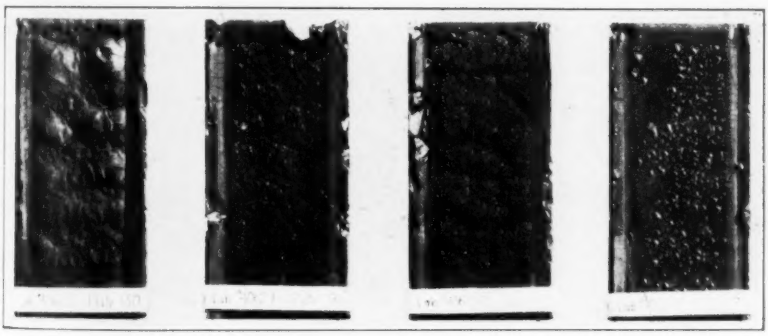


FIGURE 8.—*Accelerated tests*

Shows gradation of properties when asphalt fluxes are mixed before blowing. (See Table 2.)

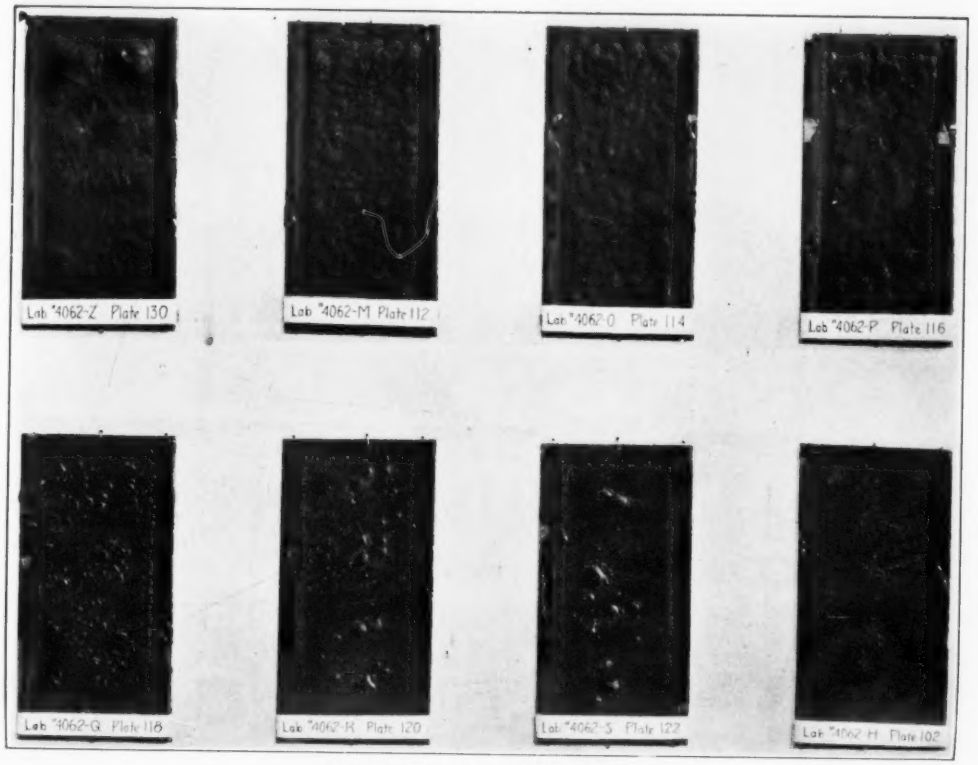

Lab. "4062-Z" Plate 130
Lab. "4062-M" Plate 112
Lab. "4062-O" Plate 114
Lab. "4062-P" Plate 116
Lab. "4062-Q" Plate 118
Lab. "4062-R" Plate 120
Lab. "4062-S" Plate 122
Lab. "4062-H" Plate 102

FIGURE 9.—*Accelerated tests.*

by changing the method of manufacture the crude oil can be made to produce asphalts that approach the appearance and behavior of other asphalts. In such cases it becomes difficult to detect the geographical origin of the crude oil from which the asphalt was made.

In Table 2 are listed the physical characteristics of mixtures of asphalts of the types A and B and their behavior in the accelerated cycle. These asphalts were prepared by mixing fluxes of type A and type B and then oxidizing them to the desired melting points. As seen in photographs of Figure 8, the behavior shows a gradation of properties from type A to type B.

TABLE 2.—*Physical constants of asphalts*

Plate No.	Material	Melting point	Penetration	Ductility	Characteristic behavior to accelerated weathering	Remarks
		°F.				
130	Type A	221	13	4.0	Type A (heavily grooved).	Shows gradation of properties from straight type A asphalt to straight type B. The fluxes were first mixed and then oxidized.
96	50 per cent type A flux; 50 per cent type B flux.	236	16	2.2	Combination of type A and B.	
92	70 per cent type B flux; 30 per cent type A flux.	217	16	2.6	do	
90	Type B	228	19	2.1	Type B	

In Table 3 the samples were prepared by mixing a flux of type A with a preoxidized asphalt of type B. Comparing panel No. 120 (fig. 9), with panel No. 92 (fig. 8) some differences in behavior are shown between mixtures of preoxidized fluxes and asphalts prepared by the oxidation of mixed fluxes. Panel No. 92 shows a behavior characteristic of a combination of types A and B, whereas the same percentage composition of A and B of panel No. 120 (but preoxidized) shows up as type B.

TABLE 3.—*Physical constants of asphalts*

Plate No	Material	Melting point	Penetration	Ductility	Characteristic behavior to accelerated weathering	Remarks
		°F.				
130	Type A	221	13	4.0	Type A (heavily grooved).	These samples are mixtures of preoxidized asphalts. The asphalt present in greatest proportion determines the "type."
112	20 per cent type B; 80 per cent type A.	216	15	3.6	Type A	
114	30 per cent type B; 70 per cent type A.	215	16	3.4	do	
116	40 per cent type B; 60 per cent type A.	214	18	3.3	do	
118	60 per cent type B; 40 per cent type A.	230	19	2.7	Type B	
120	70 per cent type B; 30 per cent type A.	235	19	2.3	do	
122	80 per cent type B; 20 per cent type A.	244	20	2.1	do	
102	Type B	272	22	1.4	do	

From this it would seem that oxidation of mixed fluxes produces an asphalt with characteristics of both fluxes, whereas in the case of mixtures of preoxidized asphalts the oxidized component present in greatest proportion determines the "type." This latter case is

illustrated in Figure 9. Whether such behavior will always be found when mixing asphalts, only further investigation will show.

Some asphalts when exposed to the accelerated weathering cycle groove and contract. Similar results are obtained on outdoor exposures. (Compare center panels, fig. 3, and panel 130 of fig. 8.) In some cases this contraction is slight, in others pronounced. A pronounced case of this contraction and upheaval is shown in Figure 5, panel No. 1, lower row.

To determine whether the aluminum base caused this behavior, similar panels were prepared from invar metal, copper, pyrex glass, and saturated asphalt felt. Upon exposure to the cycle, the behavior in all cases was the same as on the aluminum.

To show that such contraction is due to the nature of the asphalt two samples were prepared in a small laboratory still. The crude was reduced for sample A to a specific gravity of 0.983 and for sample B to a specific gravity of 1.024. These residuums were then blown to a melting point of 200° F. In this manner two different asphalts prepared from the same petroleum base were obtained. Upon exposure to the accelerated cycle, sample B showed considerably more contraction than sample A. In Figure 5, the first panel of the lower row shows a pronounced case of such contraction as a result of the method of refining. In Figure 3, the center panels show contraction as a result of improper blending.

One of the important problems confronting the asphalt technologist is that of blending various asphalts to produce mixtures best adapted for the special purposes for which they are intended. This requires an intimate knowledge of the nature and behavior of the various materials and from the above experiments it would seem that such knowledge can best be acquired by use of the accelerated cycle.

The quantitative measure of the relative durability of an asphalt is regarded as the time required (usually 20 to 80 cycles) for the asphalt to crack down to the aluminum panel. If desired, the "electrical conductivity test" described by Walker and Hickson [3] may be used to determine cracking of the asphalt to the surface of the aluminum. For the present tests this method was not used, but the panels were studied by visual inspection which proved sufficient for these purposes.

Chemical analysis, according to the method of Marcusson,[4] was found to be useful in following the progress of deterioration. Asphalts consist of oils, resins, and asphaltenes, and upon weathering the content of oil and of resin decreases, whereas the asphaltene content increases.

In Table 4 the changes that take place in asphalts on weathering are indicated. Thus, the stage and rate of deterioration of asphalt may be determined by chemical analysis.

TABLE 4.—*Chemical analyses of asphalts*

Sample	Exposure to cycle	Asphaltenes	Resins	Oils
		Per cent	*Per cent*	*Per cent*
220° F. M. P. asphalt	None (original asphalt)	26.2	4.8	68.0
	21 days	34.6	1.2	64.4
	80 days	40.6	1.2	56.6

[3] See footnote 2, p. 247.
[4] Herbert Abraham, Asphalts and Allied Substances, 3d ed., p. 755.

The value of such chemical analysis is the greater in that it will permit a definite comparison between outdoor and accelerated weathering.

VI. SUMMARY

The experiments have demonstrated that similar results are obtained when asphalts are exposed to the accelerated cycle and to outdoor weathering.

It was found that asphalts show a characteristic behavior when exposed to the accelerated cycle, so that it is possible to classify the asphalts into "types of behavior."

It was further shown that some grades of asphalts contract when exposed to the cycle, as well as outdoors.

The value of the chemical analysis of asphalts to determine progress of change was indicated.

WASHINGTON, February 1, 1930.

CONDUCTIVITY AND DENSITY OF CHROMIC ACID SOLUTIONS

By H. R. Moore and W. Blum

ABSTRACT

The conductivity and density of chromic acid solutions were determined for concentrations up to 10 molar (1,000 g/l of CrO_3). The density is practically a linear function of concentration. The conductivity increases to a maximum at about 5 molar and then decreases.

CONTENTS

	Page
I. Introduction	255
II. Preparation of solutions	256
1. Purification of chromic acid	256
2. Methods of analysis	257
(*a*) Preparation of samples	257
(*b*) Insoluble	257
(*c*) Sulphate	258
(*d*) Alkali salts	258
(*e*) Chromic acid	258
(*f*) Trivalent chromium	258
(1) Differential titration	258
(2) Direct precipitation	259
III. Conductivity measurements	259
1. Apparatus and method	259
2. Determination of cell constants	260
IV. Density measurements	260
V. Results obtained	261
VI. Conclusions	263

I. INTRODUCTION

This study is a step in an investigation of the theory of chromium plating. The solutions used in this process have chromic acid as their principal constituent. In addition, they contain some other anion, such as the sulphate ion, which is introduced as sulphuric acid or as a sulphate. During operation there is always formed in the bath some trivalent chromium, commonly supposed to exist as "chromium chromates" of undefined composition. The ultimate purpose of this research is to determine the form and function of the sulphate and trivalent chromium in such solutions. The effects of these constituents upon the density and conductivity of chromic acid will be measured to see whether they throw light on this problem. First, however, it was necessary to determine the density and conductivity of pure chromic-acid solutions to serve as a basis of reference. This report is confined to the latter measurements.

The only values found in the literature for the conductivity of chromic acid are those of Walden [1] for dilute solutions, and of Jones [2]

[1] Z. physik. Chem., **2**, p. 71; 1888.
[2] Am. Chem. J., **34**, p. 334; 1905.

for solutions from 0.8 to 7 *M* at 0° C. As no temperature coefficients were determined by Jones, the conductivities at higher temperatures could not be accurately computed. In this study the conductivities of chromic-acid solutions from 0.1 to 10 *M* were measured at 0°, 25°, and 45° C.

The densities of chromic-acid solutions, determined by several investigators, have been summarized by J. A. Beattie.[3] The data there given are for the densities at 15° C. of solutions containing from 1 to 60 per cent of CrO_3 (that is, from about 0.1 to 10 *M*). In this investigation the densities of solutions from 1 to 10 *M* in CrO_3 have been measured at 25° C., and a few values have been determined at other temperatures in order to estimate the temperature coefficients of density.

II. PREPARATION OF SOLUTIONS

1. PURIFICATION OF CHROMIC ACID

As a result of the demand in recent years for chromic acid for use in chromium plating, a product of relatively high purity is now available commercially. This material usually contains about 99.5 per cent of CrO_3 and small amounts of insoluble matter, sulphate, alkali salts, and trivalent chromium. The content of these impurities can be reduced by recrystallization, but it is difficult to remove them entirely. It was not found possible to completely eliminate trivalent chromium. In fact, unless precautions are used in the purification, there is a possibility of increasing the content of trivalent chromium, either through introduction of dust, or reducing gases from adjacent burners, or through local superheating of the solution or crystals. As will be shown, trivalent chromium is an especially objectionable impurity as it reduces the conductivity more than in proportion to its concentration. Efforts to reduce the content of trivalent chromium by evaporating in a stream of purified air or in a vacuum resulted in no marked improvement. By electrolysis with a platinum anode and a platinum cathode in a porous clay cup, the content of trivalent chromium could be reduced, as found by H. S. Lukens,[4] but not entirely eliminated.

After numerous trials it was found that the best product was obtained by dissolving the chromic acid in water, filtering through a porous porcelain filter, and evaporating on a steam bath until, on cooling, about half of the chromic acid crystallized out. The crystals were collected on a Büchner funnel. It was not necessary to thoroughly dry the product, which was used to prepare strong stock solutions from which the other solutions were then made. Two lots of chromic acid were thus purified. Analyses of the original and recrystallized acids (all dried at 110° C.) yielded the results shown in Table 1.

Inspection of these results shows that by one recrystallization the sulphate and insoluble matter were reduced to negligible concentrations. The content of "alkali salts" represents that of alkali ($Na_2O + K_2O$) combined as sulphate and chromate, chiefly the latter in the purified product. Sodium chromate contains only about 38 per cent of Na_2O, of which, therefore, the recrystallized acid contains

[3] International Critical Tables, **3**, p. 69.
[4] Trans. Am. Electrochem. Soc., **53**, p. 491; 1928.

not more than 0.04 per cent. The only significant impurity in the purified chromic acid is the trivalent chromium, of which lot B contains nearly three times as much as A. As it was not found practicable to prepare chromic acid with less Cr_2O_3 than in A, this lot was used in most of the measurements. Lot B was used in a few cases as a check upon the effect of trivalent chromium.

TABLE 1.—*Purification of chromic acid*

	Lot A		Lot B	
	Original	Recrystallization	Original	Recrystallization
CrO_3	99.49	99.75	99.37	99.74
Cr_2O_3	.22	.11	.40	.29
SO_4	.10	.01	.08	.01
Alkali salts	.18	.10	.15	.08
Insoluble	.21	.02	.17	.01
Total	100.20	99.99	100.17	100.13

2. METHODS OF ANALYSIS

In the analysis of the chromic acid before and after purification, and of the solutions used for making the density and conductivity determinations, the following methods were used.

(a) PREPARATION OF SAMPLES

The samples of solid CrO_3 were dried by heating to constant weight (usually for several hours) at 110° to 120° C. That this procedure removed practically all the water was shown by heating a sample of the same material to 120° C. in a current of dry air until constant weight was obtained and then heating it to a high temperature until the CrO_3 was entirely decomposed. The water evolved in the second heating and collected in a phosphorus pentoxide tube was equivalent to only 0.01 per cent of the weight of the sample.

The solutions for the measurements of conductivity and density were prepared and standardized on a volumetric basis with a precision of at least 1 part in 500. This procedure was used because of the greater convenience, and the fact that subsequent determinations of the effects of other constituents may be more readily interpreted on a volume concentration than a weight concentration basis.

(b) INSOLUBLE

The sample (5 to 25 g) was dissolved in water and the solution was filtered through asbestos on a Gooch crucible, previously dried at 130° C. The residue was washed with dilute hydrochloric acid (1:5) and then with water, dried at 130° C. and weighed. No attempt was made to determine the composition of the residue, part of which was a black powder, insoluble in concentrated nitric or hydrochloric acid. The treatment with dilute hydrochloric acid was used to remove any Cr_2O_3 (or chromium chromate) which might dissolve in preparing the more concentrated solutions of chromic acid. To some extent, therefore, this definition and method of determining "insoluble matter" is arbitrary.

(c) SULPHATE

The sulphate was determined in 5 to 10 g samples of CrO_3 by the method described in B. S. Tech Paper No. 346 (1927), which involves reduction of the chromic acid with alcohol in the presence of a regulated excess of hydrochloric acid, and precipitation of barium sulphate. After these analyses were completed, Willard and Schneidewind[4] showed that in this method the precipitation of barium sulphate is not complete unless the solution is allowed to stand for about 18 hours or more before filtration. They found that in the presence of acetic acid complete precipitation is much more rapidly obtained. In all of the analyses reported in this paper the solutions were allowed to stand overnight.

(d) ALKALI SALTS

The chromic acid was strongly ignited, leaving a residue consisting of Cr_2O_3 plus any alkalis ($Na_2O + K_2O$) that were present. In the residue, the latter were combined with SO_3 so far as this sufficed, and then with CrO_3 to form Na_2CrO_4 or K_2CrO_4. The green residue of Cr_2O_3 was extracted with hot water, and the filtrate evaporated to dryness. The salts thus obtained were usually contaminated with undecomposed CrO_3 and finely divided Cr_2O_3 that passed through the filter in colloidal form. The first residue was therefore ignited strongly and again extracted. The final residue, which was white or yellow, was weighed and reported as "alkali salts." No attempt was made to determine its content of Na_2O and K_2O.

(e) CHROMIC ACID

The content of Cr^{VI} was determined electrometrically by titration with ferrous sulphate. A 3,000-ohm rheostat and portable galvanometer were used. The platinum wire electrode and the tip of a calomel electrode were introduced into the beaker containing the chromic acid. A permanent deflection of 1 mm was produced at the end point by an addition of 0.02 ml of 0.1 *N* ferrous ammonium sulphate. As about 40 ml of the latter solution was used in each titration, a precision of 1 part in 2,000 was attainable. In order to attain this precision in the analysis of the solid chromic acid, the titrations were made with weight burettes. As indicated above, the concentrations of the chromic-acid solutions were determined with volume burettes.

The ferrous ammonium sulphate solution was standardized daily against a 0.1 $K_2Cr_2O_7$ *N* solution. The latter was prepared from potassium dichromate that was recrystallized from water and dried.

(f) TRIVALENT CHROMIUM

(1) *Differential titration.*—This method, described in B. S. Tech. Paper No. 346, depends upon (*a*) titration of the Cr^{VI} originally present and (*b*) titration of the total Cr^{VI} after any Cr^{III} has been oxidized. This oxidation was conducted with ammonium persulphate in the presence of silver nitrate. The Cr^{III} originally present was computed from the difference between these two titrations. It was found that the method is reliable and convenient for relatively large concentrations of Cr^{III}, but like all such differential titrations, it is not suitable for determining small amounts of Cr^{III}, especially if these are of the same order as the reproducibility of each titration.

[4] Trans. Am. Electrochem. Soc., **56**, p. 333; 1929.

(2) *Direct precipitation.*—A slight excess of ammonium hydroxide was added to the diluted solution of chromic acid, which was boiled for some time and kept slightly alkaline by small additions of ammonia. The precipitate of chromic hydroxide was filtered and washed, dissolved in dilute nitric acid, and reprecipitated with ammonia. This treatment was repeated until no tests for chromate (with lead acetate) could be obtained in the filtrate. The precipitate was ignited and weighed as Cr_2O_3.

No attempt was made to define exactly the optimum conditions for this precipitation and ignition. Tests made by this method and by differential titration upon chromic acid containing 0.5 to 5 per cent of Cr_2O_3 showed good agreement. Direct precipitation was used for concentrations of Cr_2O_3 below 0.5 per cent for the above-mentioned reasons.

III. CONDUCTIVITY MEASUREMENTS

1. APPARATUS AND METHOD

A Kohlrausch slide-wire (Leeds & Northrup) with extension coils and a 3-dial resistance box were used. An alternating current with a frequency of 1,000 cycles was supplied by a microphone hummer (General Radio Corporation) with an output of 0.06 watt when set for high intensity. This power was too low to secure a sharp minimum on the bridge, consequently the telephone current was increased fiftyfold by means of a 2-stage vacuum tube amplifier.[6] The interval of silence on the slide-wire was thereby decreased from 3 divisions to 0.1 division, thus yielding a precision of about 1 part in 3,000.

The conductivity bridge was made symmetrical by having the lead wires of equal length to the resistance box and conductivity cell. These conductors consisted of double-stranded No. 12 copper wire, inclosed in a grounded metal-sheathed cable. In other respects, the recommendations of E. W. Washburn [7] were followed. In order to eliminate the effects of any asymmetry in the arrangement or in the sine wave, a reversing switch was included in the circuit. Readings taken with the two positions of the switch did not usually differ by more than 1 part in 2,500. The mean of the two readings was used.

The integrity of the bridge assembly was confirmed by substituting a calibrated a. c. resistance box for the electrolytic cell. Values of the resistance computed from the bridge settings agreed within 1 part in 2,000 with the standard values over the range from 75 to 900 ohms.

Baths containing an oil of low viscosity and motor-driven stirrers were kept at 25° and 45° C., respectively, by means of "metastatic" mercury regulators. During the summer a cooling coil was used in the 25° bath. The heating elements were operated by relays actuated by a 3-electrode tube.[8] The Beckmann thermometers used for setting the regulators were calibrated for total immersion. The application of emergent stem corrections showed that the true bath temperatures were 24.98° C. ±0.02°, and 44.96° C. ±0.02°. As the divergences of the true temperatures from 25° and 45° C., respectively,

[6] Similar to that used by Hall and Adams, J. Am. Chem. Soc., **41**, p. 1515; 1919.
[7] J. Am. Chem. Soc., **38**, p. 2452; 1916; Leeds & Northrup Catalogue, No. 48, p. 24; 1919.
[8] Beaver and Beaver, Ind. Eng. Chem., **15**, p. 359; 1923.

produced effects smaller than the reproducibility of the conductivity measurements, the results have been reported as for 25° and 45° C. Finely shaved ice was used to secure the temperature of 0° C. used in some of the measurements.

Washburn type C cells with platinized electrodes were used. The heat transfer from these cells is very efficient, and their change in temperature during passage of the bridge current for a few minutes was less than the fluctuations in bath temperature. Hence, it was unnecessary to wait any appreciable time before making the final readings.

2. DETERMINATION OF CELL CONSTANTS

As most of the solutions of chromic acid to be used were relatively concentrated and had high conductivities, it was necessary to determine the cell constant with a solution of comparably high conductivity. For this purpose sulphuric acid of maximum conductivity was selected. The density and concentration of such acid have not been very precisely defined. Klohrausch and Holborn[9] specify 30 per cent sulphuric acid, with a density of 1.223 at 18° C. In International Critical Tables the density of 30 per cent sulphuric acid is given as 1.2150 at 25° C. The value of 0.8242 reciprocal ohm-cm is given by Eastman[10] as the specific conductivity at 25° C. of sulphuric acid with maximum conductivity. Using this value, a cell constant of 86.98 was obtained for cell A, as the average of closely concordant determinations with solutions of sulphuric acid ranging in density at 25° C. from 1.2180 to 1.2243. In like manner for cell B a constant of 63.15 was obtained.

The above values were checked approximately by means of "demal" potassium chloride solution, prepared according to Parker and Parker,[11] and with 1 *N* potassium chloride solution prepared according to Kohlrausch, Holborn, and Diesselhorst.[12] The potassium chloride was twice recrystallized, sintered, powdered, and heated for three hours at 150° C. Kohlrausch's solution and data yielded a cell constant for A of 87.03, and Parker's a constant of 87.10. Both of these are in fair agreement with the value of 86.98 obtained with sulphuric acid. Since the resistivities of sulphuric and chromic acid are comparable, the latter value was used. Similarly for cell B, the constant 63.15 was chosen as the correct value. The values 63.17 and 63.13, secured with the Parker and Kohlrausch solutions, respectively, were considered as checks on this result. When the conductivity of a given chromic-acid solution was measured in cells A and B, the values computed from the selected constants agreed to within about 1 part in 1,000.

IV. DENSITY MEASUREMENTS

The density determinations were made by E. L. Peffer, of this bureau. Glass sinkers, partially filled with mercury, were immersed in tall cylinders containing the chromic-acid solutions. The cylinders were kept in a bath maintained at 25 ±0.02° C. For the stronger, more viscous solutions pycnometers were used. Appropriate correc-

[9] Leitvermögen der Elektrolyte, p. 75; 1916.
[10] J. Am. Chem. Soc., **42**, p. 1651; 1920.
[11] J. Am. Chem. Soc., **46**, p. 332; 1924. A "demal" solution contains 1 equivalent in 1 cubic decimeter, not in 1 liter.
[12] Ann. Physik., **64**, p. 440; 1898. The corrected Kohlrausch conductances which were used are given in I. C. T., **4**, p. 230.

tions for the air buoyancy of the pycnometer and weights were applied. The values submitted were adjudged to be accurate to within 1 part in 2,000.

V. RESULTS OBTAINED

The data for concentration, density, and conductivity are assembled in Table 2. The concentrations in the first column are those obtained by actual analysis. A preliminary plot of these concentrations against the measured densities indicated that the relation is practically linear. The "revised concentrations" in the second column were obtained from a straight line drawn through the points in such a way as to make the average percentage deviations from the experimental concentrations as small as possible. This condition was satisfied by the equation $D=1.00644 + 0.06606\ C$, the constants of which were evaluated by plotting the function

$$F=\frac{D-1}{C} \text{ against } \frac{1}{C}$$

where D = density and C = concentration.[13]

This equation was found to represent the experimental data closely for the range 2 to 10 M. These "revised concentrations" have been used in the other tables and plots. (Densities obtained with 2 and 5 M cromic acid solutions prepared from lot B fell on this line, indicating that small concentrations of trivalent chromium exert no perceptible effect on the density.) Table 3 gives the densities and conductivities for integral volume concentrations.

TABLE 2.—*Experimental data on density and conductivity of chromic-acid solutions*

Experimental concentration mols/L at 25° C.	Revised concentration	Density, 25° C.	Conductivity (reciprocal ohm-cm)		
			0° C.	25° C.	45° C.
0.0994				0.0372	0.0467
.199				.0726	.0913
.497				.1723	.2162
.995	[1](0.995)	1.0731	0.2187	.3152	.3911
[a].501			.2846	.4287	.5285
1.972 B	1.969	1.1365		.5044	.6204
2.146	2.134	1.1474	.3581	.5345	.6561
2.504			.3905	.5752	.7078
2.995	2.998	1.2045	.4183	.6164	.7631
3.982	3.991	1.2701	.4398	.6573	.8184
4.640			.4381		
4.963	4.964	1.3344		.6621	.8341
5.055 B	5.075	1.3417	.4283	.6582	.8325
6.001	6.018	1.4040	.4195	.6397	.8152
7.028	7.011	1.4696	.3866	.5999	.7685
7.972	7.956	1.5320	.3468	.5477	.7112
8.939	8.937	1.5968	.2928	.4796	.6306
9.791	9.759	1.6511		.4215	.5522

[a] As the linear relation between concentration and density does not hold below about 2 M, the equation given in the text does not apply to this concentration or to others below 2 M.

[13] International Critical Tables, 3, p. 52.

TABLE 3.—*Interpolated data on density and conductivity of chromic-acid solutions*

Concentration mols/L at 25° C.	Density, 25° C.	Conductivity (reciprocal ohm-cm)		
		0° C.	25° C.	45° C.
1.00	1.0725	0.219	0.315	0.389
2.00	1.1383	.342	.513	.632
3.00	1.2041	.418	.616	.763
3.20	----------	.425	.628	.778
3.40	----------	.430	.639	.790
3.60	----------	.434	.647	.801
3.80	----------	.438	.653	.810
4.00	1.2699	.440	.657	.818
4.10	----------	[1].440	----------	----------
4.20	----------	.440	.659	.824
4.40	----------	.439	.661	.828
4.60	----------	.439	.662	.831
4.80	----------	.437	[1].662	.833
5.00	1.3358	.435	.662	[1].834
5.20	----------	.433	.661	.833
5.40	----------	.431	.659	.831
5.60	----------	.428	.653	.828
5.80	----------	.424	.648	.823
6.00	1.4016	.420	.641	.817
6.20	----------	.414	.633	.808
6.40	----------	.408	.626	.799
6.60	----------	.401	.618	.789
6.80	----------	.394	.609	.780
7.00	1.4674	.387	.600	.769
8.00	1.5332	.345	.545	.708
9.00	1.5990	.289	.477	.625
10.00	1.6648	.225	.402	.528

[1] Maximum.

A comparison of the density data for 25° C. with those compiled by Beattie for 15° C. shows substantial agreement. When Beattie's values for weight-concentration [14] are converted to volume concentrations, his data also fall upon a straight line, with slightly higher densities at 15° C. (as would be expected) than those here reported for 25° C. A few measurements of density at 15°, 25°, and 35° C. yielded, for M CrO_3, temperature coefficients of density of 0.00023 (15° to 25°) and 0.00032 (25° to 35°) which are very close to those of pure water (0.000205 and 0.000302, respectively). For 5 M CrO_3 the corresponding coefficients are 0.00075 and 0.00078. The differences between the density values for 15° and 25° correspond approximately to these coefficients. These differences are too small to affect the practical control of chromium-plating solutions.

In Figure 1 the conductivities have been plotted against the revised concentrations. These curves show that there is a maximum in the conductivity of chromic acid, the position of which varies with the temperature; that is, from about 4.1 M at 0° C. to 4.8 M at 25° C. and to 5.0 M at 45° C. This shift, especially from 0° to 25° C. is greater than can be accounted for on the basis of the change in density and hence in volume concentration, that is caused by the difference in temperature. It must, therefore, involve a difference in the degree or type of the dissociation of the chromic acid.

The temperature coefficients of conductivity computed from the data in Table 3 show that in the range from 25° to 45° C., such as is used in chromium plating, the average coefficient is from 1 to 1.5 per

[14] International Critical tables, 3, p. 69.

cent per °C. The temperature intervals were too great to permit accurate computation of the coefficients for small intervals.

The data in the tables and curves were all obtained with lot A of chromic acid except the few points marked *B*, which were obtained with lot B which has a trivalent chromium content nearly three times as great as A. It is not possible from these few observations to estimate closely the effects of trivalent chromium upon the density or conductivity. This will be the subject of a future investigation. A few preliminary experiments were made with solutions containing known larger concentrations of trivalent chromium, introduced as chromium hydroxide. These indicated that the decrease in conductivity produced by trivalent chromium, calculated as Cr_2O_3, is roughly three times as great as its proportional content. It is at least

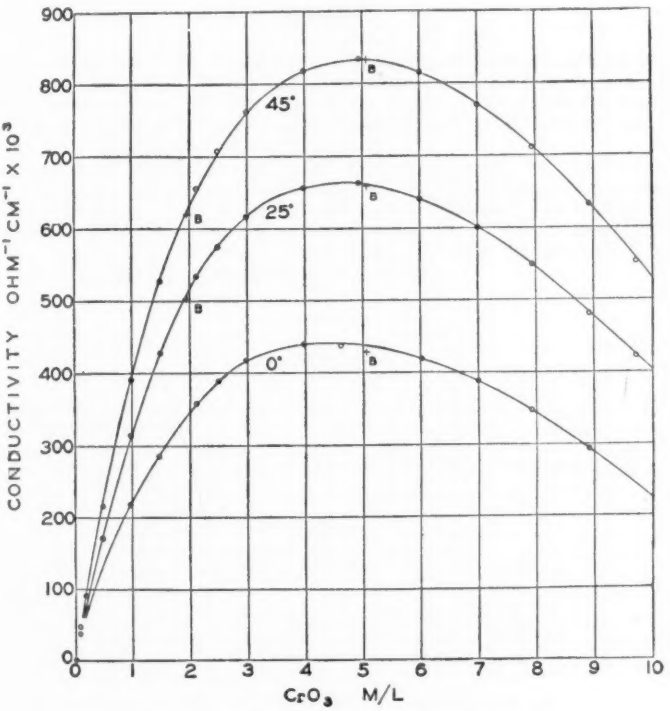


FIGURE 1.—*Conductivity of chromic acid*

possible, therefore, that the conductivities here recorded for lot A (which contained 0.11 per cent Cr_2O_3) may be too low by 0.3 per cent. Pending more exact measurements, no such correction has been applied to the data.

VI. CONCLUSIONS

The only general conclusions that can be drawn from these measurements are that (1) the density of chromic-acid solutions is practically a linear function of the volume concentration, and (2) the conductivity of chromic-acid solutions reaches a maximum at from 4 to 5 *M*, depending upon the temperature. Further experiments will be made

to determine more exactly the effect of trivalent chromium upon the conductivity. At least it is evident that the presence of a maximum in the conductivity of practically pure chromic acid shows that the curve of similar shape reported by E. A. Ollard[15] for a solution of chromic acid with a high content of trivalent chromium has no necessary bearing upon the form or function of the latter constituent in such solutions.

WASHINGTON, February 8, 1930.

[15] Electroplaters' and Depositors' Tech. Soc., 3, p. 5; 1929.

PRELIMINARY STUDIES OF THE EFFECT OF DEOXIDATION AND MOLD CONDITIONS ON THE TENSILE PROPERTIES OF CARBON STEEL CASTINGS [1]

By J. V. McCrae [2] and R. L. Dowdell

ABSTRACT

Foundrymen occasionally experience difficulties with steel castings in meeting ductility specifications of 24 per cent elongation and 35 per cent reduction of area if the steel is deoxidized with aluminum shortly before pouring the castings. Sound castings can usually be obtained in dry sand molds without the addition of "deoxidizers" immediately before pouring.

Green sand molding is generally desired but porosity, as "pinholes," often occurs. Aluminum and other "deoxidizers" studied eliminated porosity but lowered the ductility. The mold conditions are probably the important variables responsible for pinholes. A sufficient amount of "deoxidizer," however, should be in the steel at the time of pouring to deoxidize the steel from the gases evolved from the moisture contained in the mold.

CONTENTS

	Page
I. Introduction	266
II. Plan of investigation	266
1. Preliminary tests	266
2. Foundry practice used in the production of test castings	267
(*a*) Melting	267
(*b*) Molds	267
(*c*) Forms of test castings	268
(*d*) Heat treatment	268
3. Test methods and equipment	268
III. Results	268
1. Effect of varying ordinary foundry conditions	268
(*a*) Average properties of green sand castings	268
(*b*) Average properties of dry sand castings	269
(*c*) Miscellaneous variables	270
(1) Segregation	270
(2) Design of test castings	270
(3) Heat treatment	270
(4) Casting temperature	271
(5) Character of scrap used in the charge	271
(6) Alloying with either nickel or vanadium	271
2. Effect of various deoxidizers and deoxidation methods	271
(*a*) Aluminum	271
(*b*) Special "deoxidizers"	273
3. Surface treatment of green sand molds	275
4. Effect of green sand control	275
IV. Summary	276
V. Acknowledgments	277

[1] This paper gives a short account of the research work which is to be published in the Transactions of the American Society for Steel Treating, 1931.

[2] Research associate, the Steel Castings Development Bureau. (Mr. McCrae is now deceased.)

I. INTRODUCTION

The problem of obtaining sound steel castings in green sand molds with the most desirable mechanical properties has long been studied by steel foundrymen. Frequently steel foundrymen are called on to meet specifications [3] in which the minimum requirements are: Tensile strength, 60,000 lbs./in.^{2}; yield point 45 per cent of the tensile strength; elongation on a 2-inch gage length 24 per cent; and reduction of area 35 per cent.

These specifications can be generally fulfilled if dry sand or surface-dried molds are used, but green sand molds are desired in many cases. With green sand molds, it is frequently found that small holes, known as "pinholes," are frequently produced at fillets and similar positions on surfaces of castings. Most of the trouble seems to be due to the moisture in the green sand molds. These pinholes are apparently caused either by the moisture itself, as steam, or its dissociaton products or both.

While the addition of aluminum (about 1 pound per ton of steel) will usually eliminate the pinhole trouble, it will generally reduce the ductility of castings

Castings having low ductility persist even after heat treatment consisting of either normalizing or annealing from 900° to 925° C. (1,650° to 1,700° F.) followed by reheating to temperatures just below the Ac_1 critical point or about 705° C. (1,300° F.). When this problem was brought to the attention of the National Bureau of Standards, it was considered a suitable subject for study because the United States Government is a large purchaser of steel castings.

The work was undertaken, on the research associate plan,[4] in cooperation with two founder members of the organization of the association which is now known as The Steel Castings Development Bureau.

II. PLAN OF INVESTIGATION

1. PRELIMINARY TESTS

The first series of tests was planned with the aim of determining the extent of the reported difficulties. In the early plans, it was decided to study consecutive heats from the different foundries. For this preliminary work, 100 consecutive heats were produced by one of the foundries, 32 heats (not all consecutive) by a second foundry.

The seriousness of the question of low ductility was well brought out by these preliminary experiments, and on discussing this problem of low ductility in steel castings with steel mill operators, it was found that this same problem is quite common with rolled and forged steels as well as with steel castings. It was evident, therefore, that in this study of steel castings all possible phases of the subject that might influence the results should be included. With this in mind the plan of study was outlined to include the effect of varying ordinary foundry conditions, such as green and dry sand molds, miscellaneous variables, such as segregation, design of test castings, heat treatment, casting temperature, character of scrap, various deoxidizers and deoxidization methods, and various mold conditions.

[3] U. S. Navy Department Specifications 49S1G, April 1, 1925. Steel Castings (class B).
[4] Bureau of Standards Circular No. 296.

2. FOUNDRY PRACTICE USED IN THE PRODUCTION OF TEST CASTINGS

(a) MELTING

The typical melting practices used by the two foundries are shown in Table 1. These practices which did not differ materially were closely adhered to with only slight changes which will be stated as the results of this investigation are discussed. A study of Table 1 shows that the two foundries used what is considered to be the normal melting practice on steel castings.

TABLE 1.—*General foundry practices at the two acid electric steel foundries in the production of the test castings*

[All castings were poured over the lip of the ladle]

	Plants—		
	B	A	A
No. of heats	30	100	29.
Type of furnace	Heroult	Graeves-Etchell	Graeves-Etchell.
Furnace capacity (as used)	2½-ton	2-ton	2-ton.
Initial charge:			
Shop scrap (per cent)	40	40	40.
New scrap (per cent)	60	60	60.
Time:			
Melt	1 hour 10 minutes	1 hour	1 hour.
Heat	2 hours	1 hour 15 minutes	1 hour 15 minutes.
Carbon on melting (average (per cent).	0.28	0.20–0.30	0.20–0.30.
Additions:			
Iron ore	60–70 pounds with initial charge.	As needed after melting.	As needed after melting.
Lime	Usually, after melting	6 pounds before Si addition.	6 pounds before Si addition.
Carbon	As needed (as coke or pig).	As needed (as pig)	As needed (as pig).
Ferromanganese (80 per cent Mn) when added.	55 pounds 3–5 minutes before tap.	30 pounds in 2-ton ladle.	35 pounds in furnace just before tap.
Ferrosilicon (50 per cent Si) when added.	As needed, 10–20 minutes before tap.	As needed, 10–15 minutes before tap.	As needed, 10–15 minutes before tap.
Aluminum, per ton of steel.	1.2 pounds	1 pound	1 pound.
Where made	Large ladle [1]	Shank ladle [2]	Large ladle.[1]
Test pattern	2, leg	1, leg	1, leg.
Heat treatment	1,600°-1,650° F., 6 hours; furnace cool to black heat.	1,650° F., 2 hours,' soak; air cool.	1,650° F., 2 hours,' soak; air cool.

[1] Ladle contains the entire charge.
[2] Ladle contains only a part of the charge.

The commercial production of acid electric steel castings is practically a plain melting operation with no attempt to refine to the degree which is practiced with basic lined furnaces. In the production of steel castings the scrap is selected so that its phosphorus and sulphur content are usually below 0.05 per cent each. The charge is melted; brought to the desired composition by suitable additions; deoxidized, either in the furnace or the ladle or both; tapped and poured into castings.

(b) MOLDS

Both green sand and dry sand molding were used by the plants in the preparation of test castings. The green sand molding conditions were about the same in the various plants.

At various times throughout the investigation, test castings were poured in cored molds and combinations of core and green sand molds. No attempt has been made to determine the sand characteristics of

the cored molds. Also, during these experiments, various mold preparations, such as rubber compounds, alcohol, powdered aluminum, powdered magnesium, etc., were used. The results of these mold preparations are given later.

(c) FORMS OF TEST CASTINGS

All of the test castings were poured as "detached" castings. This form is not the same as the so-called "attached coupon bar." A modified form of test casting was used in the latter part of the investigation. This modification was used primarily to show how different surfaces of the same steel casting are affected by both core and green sand mold conditions.

(d) HEAT TREATMENT

Most steel foundries now heat treat their castings for commercial use in order to obtain the higher mechanical properties which the trade demands. The test castings were previously heat treated at the various foundries where they were cast. These treatments are shown in Table 1. In general, the heat treatment consisted of normalizing from 870° to 900° C. (1,600° to 1,650° F.) or annealing from the same temperature range to a black heat. Various heat treating experiments were also conducted in the course of this work with the hope of improving the ductility of the steels which had been deoxidized with aluminum.

3. TEST METHODS AND EQUIPMENT

The main test used for determining the mechanical properties of the test castings was the tensile test. Standard 0.505 inch diameter test bars were machined, after heat treating, from the test castings. The yield point was determined from the automatically drawn stress-strain curves which were determined in each case.

The Izod impact test was used to a very limited extent in a preliminary way to supplement the ductility values as measured by the tensile test. Only 16 bars were tested. The results showed that as the ductility of the castings increased there also was a slight tendency toward higher resistance to impact. However, the Izod determinations on steel castings were not considered to be discriminating enough to be of importance in this work.

III. RESULTS

1. EFFECT OF VARYING ORDINARY FOUNDRY CONDITIONS

(a) AVERAGE PROPERTIES OF GREEN SAND CASTINGS

No detailed data were available to show the chemical and physical properties and structural characteristics of the customary product in green sand castings, so a study was first made of 100 consecutive heats. The furnace charge for these consisted of about 20 per cent of boiler punchings, 15 per cent of light punchings from cold-rolled sheet, 25 per cent of heavy ball bearing punchings, and the remainder of return shop scrap (gates, heads, castings, etc.). After melting, small quantities of iron ore, lime, ferrosilicon, etc., were added as required, and after about 1 hour and 15 minutes, the metal was ready to cast. The heats were tapped into a 2-ton teapot ladle where the ferro-

manganese was added. From this ladle the metal was poured into the working ladle, the capacities of which varied from 70 to 1,200 pounds of steel. All of the test castings were poured in duplicate or triplicate from a 70-pound ladle. Aluminum (1 pound per ton of steel) was added in this ladle and the metal immediately poured into the test molds. After normalizing, these were machined into tensile bars. The customary normalizing practice used for these heats consisted of heating two hours at 900° C. (1,650° F.), followed by air cooling.

The 100 heats are grouped according to carbon contents, as shown in Figure 1. It is apparent from this figure that the carbon content must be kept at low values, say, from 0.12 to 0.17 per cent, if the majority of the heats produced under the so-called "standard" melting and normalizing practice outlined above are to meet the specification requirements.

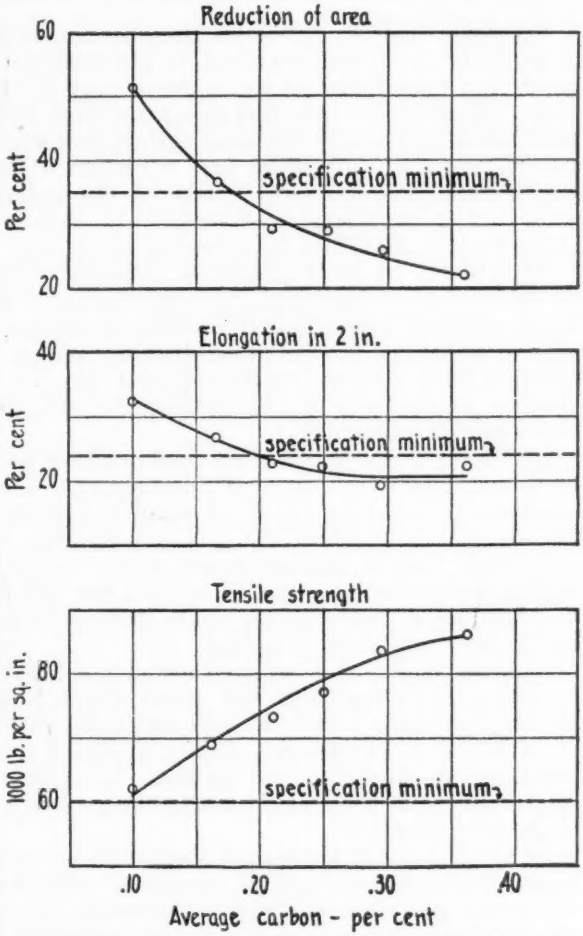


FIGURE 1.—*Relation of carbon content to mechanical properties of steel castings from 100 consecutive heats in plant production*

NOTE.—Cast steel "deoxidized" immediately before pouring with the equivalent of 1 pound of aluminum per ton of steel added to shank ladle. Test castings made in green sand holes.

(b) PROPERTIES OF DRY SAND CASTINGS

Tensile tests were made on dry sand castings selected at random from 32 heats containing approximately 0.20 to 0.30 per cent carbon. The castings were not made especially for the tests but were taken from heats made early in the course of this investigation by company "B." About one-fifth of the specimens representative of the 32 heats made by company "B" failed to meet the specification requirements of 35 per cent or more reduction of area and, in addition, about 5 per cent showed less than the required 24 per cent or more elongation in 2 inches.

Microscopic examination showed that the dendritic or Widmanstatten structure characteristic of cast steel was more easily eliminated if the steel had been cast without the addition of aluminum immediately before pouring.

(c) MISCELLANEOUS VARIABLES

(1) SEGREGATION.—Steel castings do not, in general, show so great a degree of structural, chemical, or physical homogeneity, as wrought steels and the variations encountered may be of considerable magnitude. Fractured tensile test specimens from heats originally reported to contain very nearly the same carbon, but which showed widely different values of elongation and reduction of area were selected for microscopic examination. Study of the individual test specimens indicated a considerable difference in carbon content which was subsequently confirmed by chemical analysis.

(2) DESIGN OF TEST CASTINGS.—Another factor considered relates to the form of test casting. The one regularly used had sharp corners in the portions from which the tensile specimens are machined. Such corners affect the process of dendritic formation and may introduce a line of weakness extending into the test bar. It was found that slight changes in the form of test castings did not produce noticeable differences in the ductility.

(3) HEAT TREATMENT.—Thermal analyses were made of two of the cast steels, since these normally contain somewhat higher silicon than commercial wrought steels of similar carbon contents. The Ac_1 transformation temperature was considerably higher in both of the cast steels than in the low-silicon steels usually employed for rolled and forged products. On this account the first modifications made in the "standard" normalizing cycle were to increase the temperature and decrease the rate of cooling.

Samples from heats which showed good tensile properties under "standard" normalizing and those which showed relatively poor tensile properties were quenched and subsequently tempered at 650° C. (1,200° F.). Prolonged soaking at high temperatures is helpful in breaking up dendritic segregation. Long heating at temperatures just under or in the transformation range has frequently been found to increase ductility.

Of the five variables in heat treatment investigated, only one, prolonged tempering at 1,300° F., produced quite definite and appreciable improvement in the ductility of the steels. Increase in the temperature from which the steel was cooled, combined with a slower cooling rate (furnace cooling), was not effective in increasing the ductility of the samples. Water quenching followed by tempering at 650° C. (1,200° F.) did not bring the heats having low ductility within the requirements, although either a higher tempering temperature or a longer time of tempering might have produced a sufficient improvement. The use of water quenching, in general, followed by tempering would not appear to be practicable on account of the intricate design of the average foundry product.

One type of treatment which effectively raised the ductility was a tempering at 705° C. (1,300° F.) subsequent to normalizing. There was no marked change in ductility produced by tempering those heats

which showed high elongation and reduction of area after simple normalizing, but the so-called poor heats showed a relatively large increase in both reduction of area and elongation when tempered for only two hours at 705° C. (1,300° F.).

A 15-hour heating at 705° C. (1,300° F.) produced a considerable degree of spheroidization of the cementite which was accompanied by an increase in the elongation and reduction of area, although there was no appreciable change in the dendrites which were not removed by the simple normalizing.

(4) CASTING TEMPERATURE.—The results from the 100 heats suggest that there is a tendency toward higher tensile properties if the castings are poured as hot as practicable. It was noted that results from additional heats, picked at random, were consistent with the general indications of the 100 consecutive heats previously reported.

(5) CHARACTER OF SCRAP USED IN THE CHARGE.—Several heats were made in which the character of the scrap was varied in order to study whether this factor bears any important relation to the ductility of the castings. The results indicated that the ductility of test castings poured in green sand (1 pound of aluminum per ton of metal added to the shank ladle before casting) was somewhat lower when light scrap was used in the charge rather than heavy scrap. In general, however, the question of the character of scrap used appears to play only a small part in the matter.

(6) ALLOYING WITH EITHER NICKEL OR VANADIUM.—Two of the heats containing about one-half and three-fourths per cent of nickel, respectively, showed a combination of good strength and ductility but it does not appear justifiable to attribute these properties solely to the nickel. Several of the other heats containing nickel showed very low ductility. Vanadium was also added to a 70-pound ladle of metal. This ladle of metal was divided, aluminum being added to one part but not to the other. One test bar from a casting containing 0.25 per cent V, without aluminum, showed good properties, but the corresponding bar was porous. It seems that the additions of low amounts of the usual alloy elements will not appreciably improve the ductility of steel castings made in green sand.

2. EFFECT OF VARIOUS DEOXIDIZERS AND DEOXIDATION METHODS

Numerous experiments were made to show the effect of different so-called deoxidizers on the tensile properties of steel castings when added in various ways and in different amounts. On account of the widespread use of aluminum in steel casting practice, attention was first given to the use of this deoxidizer. Later, experiments were made with other less familiar "deoxidizers." These tests should be regarded as "pilot tests." However, the general behavior of the "addition" was rather clearly indicated.

(a) ALUMINUM

In a considerable number of cases in this investigation sound castings were obtained when no aluminum was added. Indeed, the claim has been made that in normal foundry practice sound castings can be obtained without the use of aluminum for about 80 per cent of the time.

Additional heats were made in which the same amount of aluminum was added to the steel, but the addition was made to the metal in the large ladle during tapping. A comparison of the results with those obtained on the 100 heats showed that, while the ductility values were somewhat low in a number of cases, they were not so low as the values obtained with the 100 heats. It would seem that the products of deoxidation have had a better chance to rise to the surface and, perhaps, free the steel more from colloidal particles which would affect the ductility. Many of these bars, however, contained blowholes, thus showing that the steels had not completely "degasified" or that bad mold conditions had actually "regasified" the metal which did not contain sufficient deoxidizer to allow for the gases evolved by the mold. There is indirect evidence that the greater these mold gases the higher will be the amount of aluminum necessary to insure soundness and the lower will be the ductility of the steel. The practice of deoxidizing with aluminum in the large ladle does not insure soundness in those cases where the metal is to be poured into a smaller ladle in order to pour small castings.

In general, "pinholes" were prevalent in the majority of the castings in which the practice was followed of adding the aluminum in the large ladle. Although no definite conclusions are justified on the basis of these results alone, it is apparent that the problem does not depend entirely upon the time when the aluminum additions are made with respect to the time of casting. Evidently the initial condition of the steel plays an important part. In this respect, they tended to duplicate the condition which so frequently obtains in castings made from steel which has not been treated with aluminum. The porosity may have resulted from an insufficient amount of residual deoxidizer to compensate for the gases formed from the moisture of the mold.

The results of tests carried out for the purpose of studying the effect of varying the amount of aluminum added to green sand castings are given in Figure 2. Two corresponding series of tests were carried out—one in the plant of company "A," the other at company "B." In the first series the amount of aluminum added was progressively increased up to 2 pounds per ton of steel, the additions being made in the "shank" ladle (70 pounds capacity). In the companion series (not shown in fig. 2) corresponding additions were used but were made in the large (2½-ton) ladle, the aluminum being added by fastening it to the end of a steel stirring rod and holding it beneath the surface of the metal. The test castings in this case were poured in approximately 12 minutes from a 150-pound capacity ladle which had been filled by pouring over the lip from the 2½-ton ladle.

It will be noted in Figure 2 that the tensile properties corresponding to zero addition of aluminum were very noticeably superior to those of any of the steels of the same series containing aluminum. These values are not readily attainable and are regarded somewhat as ideals or standards for comparison purposes rather than as results representative of general foundry practice.

As is evident from both series of tests, a relatively small addition of aluminum to the cast steel resulted in a marked change in the ductility properties of the steel. The decrease in the ductility, however, does not bear a linear rleationship to the amount of aluminum added. Both series of tests indicated a "ductility minimum" corre-

sponding to a relatively early stage in the series of aluminum additions.

The results of both series of tests were in good agreement in showing that the effect of the progressive aluminum additions upon the tensile strength of the steel was relatively very much less than upon the ductility. In the tests in which the aluminum was added in the large ladle, test castings were poured in both green sand and core sand. No important or singificant differences were obtained in the properties of the two sets of test castings prepared in this way.

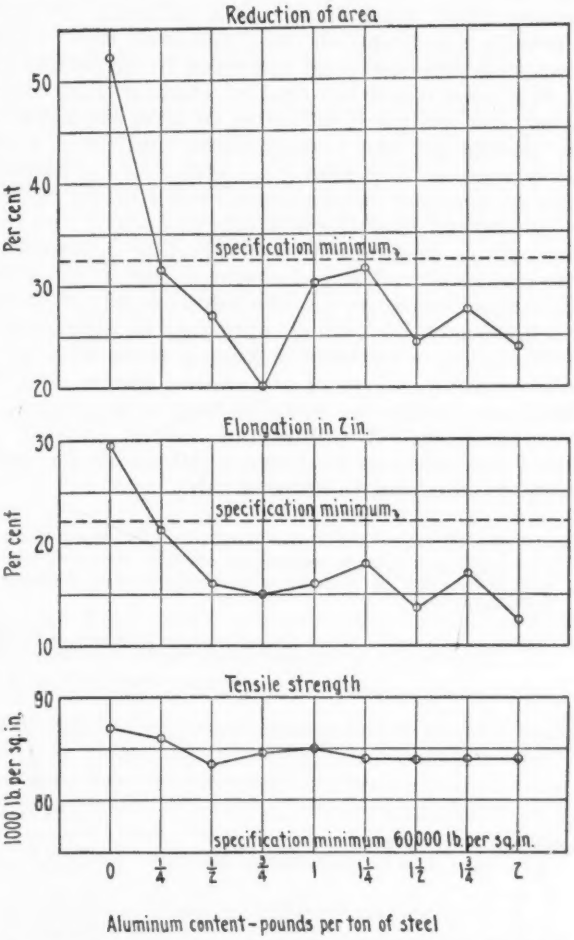


FIGURE 2.—*Effect of quantity of aluminum on mechanical properties of steel castings*

NOTE.—Heat 5,680: Analysis C 0.26, Mn 0.63, Si 0.37 per cent. Aluminum added to shank ladle immediately before casting. Test castings made in green sand molds. Normalized at 900° C. (1,650° F.) two hours. Each point represents average of two tests.

(b) SPECIAL DEOXIDIZERS

In order to determine whether sufficient deoxidation could be secured without lowering the ductility of the steel if the aluminum were in combination, tests with a number of special deoxidizers were carried out. Compounds of aluminum, silicon, and iron were first used. One of these, Alsifer, is a commercial product. Three others were prepared for the tests at the Pittsburgh station of the Bureau of Mines, under the supervision of Dr. C. H. Herty.

A composite core sand and green sand mold was used for the test castings in which the gate, the end near the gate, and two-thirds of one side of the mold were made of core sand, the balance being rammed from green sand. With such a mold one face of the casting will

illustrate the behavior of the metal in contact with green sand. At the same time the reduced section from which the tensile test bars are cut gives the properties of green-sand castings.

Some pinholes were found after chipping the casting at the fillets, but the only castings which showed an appreciable degree of porosity in the fillets were those made without the addition of aluminum. Porosity was found on the green-sand side. The same metal in contact with the core sand appeared to be perfectly sound.

While the particular heat selected for these experiments showed relatively low values of reduction of area when cast without the addition of aluminum, the results clearly indicated a reduction in the ductility upon adding aluminum either in the metallic form or as part of any of the four aluminum-silicon-iron alloys used. In general, the tests showed that the addition of each of the four aluminum-silicon-iron alloys in amounts equivalent to 1 pound of aluminum per ton of steel produced sound castings, but lowered the ductility to about the same degree as did the addition of the aluminum alone.

Other additions which appeared to offer some possible promise as a deoxidizer were tried. Among these were an alloy of manganese-silicon-boron, alloys of alumnium, silicon, and boron, of several different compositions, metallic beryllium, an iron-aluminum alloy, and ferrotitanium. A number of rather unusual additions were also used, consisting of lead, brass (80 per cent copper, 20 per cent zinc), copper, zinc, and fused soda ash.

TABLE 2.—*Effect on the tensile properties of steel test castings of a number of special deoxidizers, including aluminum, boron, boron-silicon-manganese alloy, aluminum-iron alloy, a mixture of ferrosilicon and ferromanganese, and carbon free ferrotitanium*

[All castings were made in the combination green-sand and core-sand molds. Heat, 6983; C, 0.23 per cent. Mn, 0.66 per cent, Si, 0.31 per cent; heat treated by normalizing at 900° C. (1,650° F.), 2 hours.]

Specimen No.	Additions [1]	Yield point	Tensile strength	Elongation in 2 inches	Reduction of area	Remarks
		Lbs./in.²	*Lbs./in.²*	*Per cent*	*Per cent*	
83–2	None					Porous.
2a	None					Porous.
4	1 pound Al per ton of steel (0.05 per cent Al)	35,000	70,500	30.0	46.0	Sound.
4a	1 pound Al per ton of steel (0.05 per cent Al)	36,000	69,000	30.0	46.0	Do.
6	½ pound Al per ton of steel (0.025 per cent Al)	39,000	71,000	31.0	51.5	Do.
6a	½ pound Al per ton of steel (0.025 per cent Al)	36,500	70,500	28.5	40.0	Do.
8	40 g. alloy D [2] (0.007 per cent B)	33,500	71,600	20.0	18.0	Do.
8a	40 g. alloy D [2] (0.007 per cent B)	34,500	70,000	20.0	22.5	Do.
10	Mixture of ferrosilicon and ferromanganese [3]	30,000	70,000	26.0	40.0	Do.
10a	Mixture of ferrosilicon and ferromanganese [3]	38,500	72,000	34.0	51.0	Do.
12	70 g. alloy F [2] (0.05 per cent B, 0.06 per cent Si, 0.10 per cent Mn)	38,000	62,500	6.0	6.0	Do.
12a	70 g. alloy F [2] (0.05 per cent B, 0.06 per cent Si, 0.10 per cent Mn)	39,000	67,000	10.0	10.0	Do.
14	40 g. FeAl [4] (0.06 per cent Al)	35,500	67,000	20.0	22.0	Do.
14a	40 g. FeAl [4] (0.06 per cent Al)	36,000	67,000	20.0	28.0	Do.
16	30 g. C free FeTi [2] (0.025 per cent Ti)	38,000	68,000	18.5	18.0	Do.
16a	30 g. C free FeTi [2] (0.025 per cent Ti)	39,500	68,000	19.0	21.5	Do.

[1] Additions were made in the 70-pound ladle.

[2] Chemical composition of alloys:

	Boron	Si	Mn
D	6.0	----	----
F	24.0	25.0	45.0

FeTi—approximately 28 per cent Ti.

[3] Additions equivalent of 0.05 per cent Si and 0.10 per cent Mn in the steel.

[4] FeAl made by melting 10 pounds of aluminum and placing pot on the scales, then adding 10 pounds of molten steel, allowed to cool without stirring.

Aluminum, boron, and silicon alloys of three different compositions were used, and for comparison the results obtained by adding aluminum in the ordinary manner and also the results of one series in which metallic beryllium was used as the deoxidizer. It was noted that the bars treated with the aluminum-boron-silicon alloy though sound were exceedingly low in their tensile properties while those of the beryllium-treated bars were only on a par with the aluminum treated ones.

The effect upon the tensile properties of steel castings produced by a number of special additions, including boron, a boron-manganese-silicon alloy, a mixture of ferrosilicon and ferromanganese, an aluminum-iron alloy and carbon-free ferrotitanium is shown in Table 2. Of the various additions, the mixture of ferrosilicon and ferro manganese was the only one which appeared to be promising.

The results obtained with an addition of zirconium (added as ferrozirconium to a 2½-ton ladle) of 0.10 pound per ton of steel were favorable from the standpoint of porosity, but the ductility of the steels was decreased about the same as with aluminum addition of 1 pound per ton.

3. SURFACE TREATMENT OF GREEN-SAND MOLDS

As stated at the outset, by the use of dry sand molds in steel-casting work, porosity difficulties are reduced to a minimum. A few experiments were carried out for the purpose of showing whether or not, by suitable mold preparations, the difficulties accompanying the use of green-sand molds could be overcome by eliminating or counteracting the effect of the moisture in such molds. The mold preparations used consisted of various surface treatments. It was noted that the test specimens were porous in a good many cases.

4. EFFECT OF GREEN-SAND CONTROL

From the beginning of this investigation it was believed that variables in green-sand practice, especially moisture, were largely responsible for the difficulties encountered from pinholes in most steel foundries. It was thought, however, that sand control would be harder to maintain to a high degree than would some suitable deoxidizer which might insure soundness without impairing ductility. The early work on deoxidizers, however, was not especially promising, so the effect of sand control was considered.

Instead of using a facing sand containing the usual amount of clay binder (bentonite), some of this binder was replaced by cereal bonds (corn flour and wheat flour) which varied between 0.2 and 0.6 per cent by volume, while the bentonite varied between 0.4 and 0.8 per cent. Molasses water, consisting of one part molasses to three parts of water, was used for tempering.

The tensile properties of test bars from 12 heats showed that little difficulty was encountered from porosity or low ductility when the moisture and permeability of the sand was closely controlled and when the carbon content of the heats varied between 0.18 and 0.25 per cent. The six heats from foundry "B" had higher ductility after the heat treatments than those from foundry "A." Aluminum was added in both cases, but less was added to the heats from foundry "B"; also this foundry made the additions to the large ladle by the submersion

method previously described. This allowed more efficient deoxidation and also more time for the deoxidation products to escape from the metal which may have been the reason for the increased properties.

IV. SUMMARY

1. The tensile properties frequently specified for acid electric steel castings, as minimum requirements, are an ultimate tensile strength of 60,000 lbs./in.^{2}, and an elongation in a 2-inch gage length of 24 per cent, and 35 per cent reduction of area. Test castings made in dry-sand molds usually meet these requirements, but castings often lack soundness. This difficulty is usually overcome by the addition of a deoxidizer, usually aluminum, shortly before pouring, but the test castings not infrequently fail to meet the requirements with respect to ductility. The tensile properties and soundness of test castings of acid electric steel made in several steel foundries under a variety of conditions have been studied at considerable length as a basis of an investigation of this problem.

2. A survey of the field was made by the study of 100 consecutive heats in one foundry and 32 made in another. The tendency toward low ductility is related to the carbon content of the steel. This preliminary survey indicated that if the carbon content is between 0.10 and 0.17 per cent, manganese between 0.60 and 0.70 per cent, and silicon between 0.30 and 0.40 per cent, the addition of about 1 pound of aluminum per ton of steel to the ladle shortly before pouring will not lower the ductility of the normalized castings below the usual limitation.

3. Moderate changes in the variables in ordinary acid electric steel foundry practice have little effect with respect to low ductility of the steel. The size and character of the scrap used in the charge have no appreciable effect. Additions of nickel and of vanadium in moderate amounts do not appear to improve the ductility. Heat treatment, aside from rather pronounced changes involving quenching and tempering, appeared to have no appreciable effect upon the low ductility. A higher normalizing temperature—for example, 1,100° C. (2,000° F.) instead of 900° C. (1,650° F.)—appeared beneficial. A rather high casting temperature also appears desirable.

4. Of the numerous additions used as possible deoxidizers, including ferro-alloys of boron, zirconium, silicon, aluminum, and titanium, none were superior to aluminum. Most deoxidizers used were found to have a marked effect in reducing the ductility of the steel.

5. The effect upon the ductility of steel when aluminum is added is not a linear relationship. The amount of aluminum necessary to insure soundness in green-sand molds without seriously impairing the ductility may vary for different steel according to the melting practice, the mold condition, and the state of oxidation of the steel. It is believed, however, that a sufficient amount of deoxidizer should be in the steel at the time of pouring to deoxidize the steel from the gases evolved by the green sand. Usually about one-half pound of aluminum per ton of steel in the form of metallic aluminum or as an alloy of aluminum will give sound castings which, after normalizing, will show ductility somewhat higher than the specified minimum. If aluminum is added during tapping, the castings may be somewhat porous. The addition of at least part of the aluminum immediately

before pouring is recommended. Although there is no definite proof, the inference from this work that inclusions of Al_2O_3 are largely responsible for the low ductility resulting when aluminum is added to the steel shortly before casting would seem to be justified.

6. The results of a few experiments with mold preparations in the form of surface treatments for counteracting the influence of the moisture in green-sand molds indicated that this method has merit, but the results were not especially promising.

7. The situation as regards porosity can generally be improved and the difficulties often overcome by controlling the mold conditions as regards moisture and permeability. By this method the minimum of aluminum or other deoxidizers is required to compensate for the gases evolved by the mold. If the carbon content is about 0.20 per cent, it will then be easier to meet the ductility specifications.

V. ACKNOWLEDGMENTS

The authors wish to express their appreciation and thanks to the Steel Castings Development Bureau and to George Batty, director of research of that bureau, for their interest throughout this investigation. Previous to the organization of the Steel Castings Development Bureau, the most hearty cooperation and support was given by the following persons: Clarence Tolan, jr., and C. S. Roberts, of Dodge Steel Co.; H. C. H. Cunningham and C. R. H. Cunningham, of Crucible Steel Casting Co. We also wish to express our sincere appreciation to H. S. Rawdon, chief of the division of metallurgy, and to Dr. H. W. Gillett, former chief of the division of metallurgy of the Bureau of Standards, for their helpful suggestions; to H. J. French, formerly of the Bureau of Standards, for directing the early part of the investigation; to the metallurgical staff as a whole, but more especially to H. K. Herschman, S. J. Rosenberg, L. Jordan, and C. M. Saeger, jr. We also wish to extend our appreciation to Dr. C. H. Herty, jr., and J. M. Gaines, jr., of the Bureau of Mines, for cooperation and helpful suggestions.

WASHINGTON, April 1, 1930.

THE PRECIPITATION AND IGNITION OF MAGNESIUM AMMONIUM PHOSPHATE

By J. I. Hoffman and G. E. F. Lundell

ABSTRACT

Conditions that are necessary for the precipitation and ignition of magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, in determinations of phosphorus or magnesium are described, and the temperatures at which the precipitates should be heated to obtain the most reliable results have been determined. In addition, observations on the temperatures of platinum crucibles heated over Tirrill, Méker, or Fischer burners with the same gas are reported, as well as observations on the losses in weight of platinum crucibles at different temperatures.

CONTENTS

	Page
I. Introduction	279
II. Determination of phosphorus	280
1. Preparation of a standard solution of silver phosphate	280
(*a*) Tests for purity of the reagents and of silver phosphate	281
2. Analysis of silver phosphate	281
(*a*) Determination of silver as chloride	281
(*b*) Determination of phosphorus by the pyrophosphate method (recommended procedure)	282
(1) Solubility of magnesium ammonium phosphate in the determination of phosphorus	284
(2) Ignition of magnesium ammonium phosphate in the determination of phosphorus	284
III. Determination of magnesium	286
1. Preparation of a solution of magnesium chloride	286
2. Standardization of the solution of magnesium chloride	287
(*a*) Determination of magnesium by weighing as the oxide	287
(*b*) Determination of magnesium by weighting as the sulphate	287
(*c*) Determination of magnesium by weighing as the pyrophosphate (recommended procedure)	287
(1) Solubility of magnesium ammonium phosphate in the determination of magnesium	288
(2) Ignition of magnesium ammonium phosphate in the determination of magnesium	289
IV. Summary	293

I. INTRODUCTION

In 1825 Berzelius [1] mentioned magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, as a very insoluble substance. Since that time the compound has been extensively used in determinations of magnesium and of phosphorus. In either case the precipitate is usually ignited and weighed as magnesium pyrophosphate, $Mg_2P_2O_7$. The vast amount of literature indicates that there is some conflict of opinion concerning the conditions necessary to obtain a precipitate which, when ignited, will yield a compound exactly conforming to the formula, $Mg_2P_2O_7$.

[1] J. J. Berzelius, Poggendorff's Annalen, 4, p. 275; 1825.

The present investigation was undertaken in order to determine these conditions by analyzing specially prepared solutions which contained known amounts of phosphorus in the one case and magnesium in the other. Special attention was given to the temperature at which the precipitates were ignited. The effects of different amounts of ammonium hydroxide and ammonium chloride have been so completely discussed by Gooch and Austin,[2] by Epperson [3] and others that they need not be taken up here. Only the simple procedures which have been found to give accurate results will be discussed.

II. DETERMINATION OF PHOSPHORUS

Gooch and Austin used recystallized disodium hydrogen phosphate as the phosphorus standard in their work on the effect of ammonium hydroxide and ammonium salts. Epperson found very good agreement between the results for phosphorus obtained by a double precipitation as magnesium ammonium phosphate and those obtained by a method in which the phosphorus was precipitated as silver phosphate, the latter being taken as the standard. McCandless and Burton[4] recommended the use of microcosmic salt, $NaNH_4HPO_4{\cdot}4H_2O$, as a standard. In the present work it was deemed desirable to start with pure silver phosphate as a fundamental standard because Baxter and Jones [5] have shown that this salt can be easily prepared in a perfectly definite and pure state.

1. PREPARATION OF A STANDARD SOLUTION OF SILVER PHOSPHATE

The method given by Baxter and Jones for the preparation of their samples N and O, was employed for the preparation of the silver phosphate in the present work.[6] The precipitates (corresponding to samples N and O) were transferred to large platinum dishes and washed at least twenty times by decantation with distilled water. The washing was continued over a period of 40 hours in order to allow ample time for the leaching of all soluble matter. After draining the precipitates as much as possible on papers they were transferred to tubulated platinum crucibles and ignited to constant weight at 450° to 500° C. A stream of dry, purified air

[2] F. A. Gooch and Martha Austin, Chem. News, **79**, p. 255; 1899.
[3] Alice Whitson Epperson, J. Am. Chem. Soc., **50**, p. 321; 1928.
[4] J. M. McCandless and J. I. Burton, Ind. Eng. Chem., **16**, p. 1267; 1924; **19**, p. 406; 1927.
[5] G. P. Baxter and G. Jones, J. Am. Chem. Soc., **32**, p. 298; 1910.
[6] This method is as follows:
"A 0.03 normal solution of silver nitrate was slowly poured into a 0.03 normal solution of disodium hydrogen phosphate with frequent shaking. This reaction may be roughly considered to take place in two stages represented by the equations:

$$3AgNO_3+2Na_2HPO_4=Ag_3PO_4+NaH_2PO_4+3NaNO_3$$
$$3AgNO_3+NaH_2PO_4=Ag_3PO_4+NaNO_3+2HNO_3$$

"At the beginning of the precipitation the solution is very slightly alkaline, and remains very nearly neutral during the addition of the first half of the silver nitrate. The concentration of the silver ion is kept very low by the excess of phosphate, and therefore little occlusion of the acid salts is to be expected in spite of the fact that the solution contains appreciable concentrations of the monohydrophosphate and dihydrophosphate ions. The precipitate during this stage is very finely divided and does not settle well, and therefore no attempt was made to collect it separately.
"During the addition of the second half of the silver nitrate the solution becomes slightly acid and the solubility of the silver phosphate increases rapidly. The precipitate settles readily. During the second stage the conditions are more favorable for the occlusion of the acid phosphate, but only a small amount of silver phosphate is precipitated during this stage.
"After standing a short time the mother liquor was decanted from the precipitate (sample N), and exactly the calculated amount of redistilled ammonia, diluted to 1 liter, was added to neutralize the excess acid and complete the precipitation. Since this sample (sample O) was evidently produced from a solution which was slightly acid at the beginning of the precipitation, although very nearly neutral at the end, and since it contained a considerable amount of silver, the conditions were favorable for the formation of acid salts."

was passed over the silver phosphate during the ignition. After the samples had been cooled in a desiccator over sulphuric acid, portions of each were taken and the silver determined as chloride. The results checked exactly. The two samples of silver phosphate were accordingly combined and used for preparing the standard solution.

The composite sample (9.5057 g) was dissolved in 100 ml of dilute nitric acid (15 : 85),[7] transferred to a weighed liter flask, diluted to approximately 1 liter, and again weighed. The weight of the solution was 999.61 g. One gram, therefore, contained 0.009509 g of silver phosphate, which is equivalent to 0.002529 g of magnesium pyrophosphate. All stoichiometric computations were based on the 1925 International Atomic Weights.

(a) TESTS FOR PURITY OF THE REAGENTS AND OF SILVER PHOSPHATE

Tests for purity of the reagents and of silver phosphate were as follows: The silver nitrate showed no chloride when it was dissolved and slightly acidified with nitric acid. In neutral solution no precipitate formed, thus showing the absence of arsenic and vanadium. The disodium hydrogen phosphate showed no trace of chloride when tested with silver nitrate in dilute nitric acid solution. Tests with hydrogen peroxide in nitric acid solution showed that vanadium was absent. A test with potassium thiocyanate in dilute acid solution showed the absence of iron. The absence of a precipitate after the neutral solution had stood for 12 hours indicated freedom from any appreciable amount of aluminum. Saturation with hydrogen sulphide in either acid or ammoniacal solution gave neither a precipitate nor a coloration. The tests of silver nitrate and disodium hydrogen phosphate were made on 10 g samples.

The silver phosphate showed no trace of nitrates when tested with diphenylamine and no chloride when it was dissolved in dilute nitric acid and treated with silver nitrate. The residue insoluble in dilute nitric acid mentioned by Baxter and Jones was visible, but amounted to only 0.4 mg in a 2.0 g sample.

2. ANALYSIS OF SILVER PHOSPHATE

(a) DETERMINATION OF SILVER AS CHLORIDE

Portions of the solution of silver phosphate were transferred to beakers by means of weight burettes, and the silver was precipitated by adding hydrochloric acid in such excess that the solution contained 1 per cent of the acid by volume (1 ml of HCl, specific gravity 1.19, per 100 ml of solution). The precipitates were coagulated by digesting on the steam bath for one-half hour, after which the solution was cooled and allowed to stand overnight. The precipitates were collected in perforated platinum crucibles fitted with platinum pads (Munroe rucibles), washed with dilute hydrochloric acid (1:99), dried at 140° C., cooled, and weighed. The filtrates and washings showed not the slightest turbidity. The precipitates showed no occlusion of phosphate. In all operations involving the preparation

[7] This denotes 15 ml of concentrated nitric acid (specific gravity 1.42) mixed with 85 ml of water. This system of designating dilute acids is used throughout this paper. If no dilution is specified, the concentrated reagent is intended. Ammonium hydroxide (1 : 19) denotes 1 volume of NH_4OH (specific gravity 0.90) mixed with 19 volumes of water,

of silver phosphate and the precipitation of silver chloride the solutions and precipitates were carefully protected from light.[8] Table 1 shows the results obtained in the determination of silver in the standard solution of silver phosphate.

TABLE 1.—*Results found in determinations of silver in silver phosphate*

	AgCl	
	Calculated from weight of Ag_3PO_4	Found
	g	*g*
1	0.7018	0.7020
2	.7681	.7678
3	.7844	.7844
4	.7648	.7645
5	1.2352	1.2352

(b) DETERMINATION OF PHOSPHORUS BY THE PYROPHOSPHATE METHOD (RECOMMENDED PROCEDURE)

The conditions under which phosphorus must be precipitated by magnesia mixture so as to obtain a residue of the correct composition upon ignition have been described by the authors [9] and by Epperson.[10] The results obtained, however, were not checked against carefully prepared standards as is done in the present work. The recommended procedure is as follows: To the neutral or faintly acid solution of phosphorus as orthophosphate, containing 0.2 g of P_2O_5 or less, add 5 to 10 ml of hydrochloric acid. Adjust the volume of the solution to 125 to 150 ml, and add 10 ml of acid magnesia mixture[11] per decigram of P_2O_5, never less than 10 ml in the first precipitation, cool in ice water, and add ammonium hydroxide slowly and with vigorous stirring until the solution is slightly alkaline to litmus. Stir for a few minutes or until the precipitate is well formed, and then add 5 to 10 ml of ammonium hydroxide. Let stand for at least four hours, preferably overnight, filter, and wash with dilute ammonium hydroxide (1:19). Dissolve the precipitate in 50 ml of warm dilute hydrochloric acid (1:9), wash the paper thoroughly with hot dilute hydrochloric acid (1:99), dilute the solution to 125 to 150 ml, add 2 to 3 ml of acid magnesia mixture, cool in ice water, and again precipitate the phosphate by the above procedure. Allow to stand for 4 to 24 hours, filter on a paper of close texture, and wash with dilute ammonium hydroxide (1:19). Transfer the precipitate and paper to a weighed platinum crucible, char the paper without flaming, burn off the carbon at a temperature below 900° C.,[12] and finally ignite to constant weight, preferably in a muffle, at 1,050° to 1,100° C.[13]

[8] That this is necessary is shown in an article on The Effect of Light on Silver Chloride in Chemical Analyses, by G. E. F. Lundell and J. I. Hoffman, B. S. Jour. Research, **4** p. 109; 1930.

[9] Ind. Eng. Chem., **15**, pp. 44 and 171; 1923; and J. Assoc. Official Agri. Chem., **8**, p. 184; 1924.

[10] See footnote 3, p. 280.

[11] Acid magnesia mixture is prepared as follows: Dissolve 50 g of $MgCl_2 \cdot 6H_2O$ and 100 g of NH_4Cl in 500 ml of water, make slightly ammoniacal, allow to stand overnight, and filter. Acidify the filtrate with hydrochloric acid, add 5 ml of the acid in excess, and dilute to 1 liter.

[12] K. D. Jacob and D. S. Reynolds, J. Assoc. Official Agri. Chem., **11**, p. 128; 1928; have shown that phosphorus is lost if $Mg_2P_2O_7$ is ignited with carbon at or above 900° C.

[13] If precipitates are not too large (<0.25 g) and have been obtained by the recommended procedure, satisfactory results can be had by igniting at 1,000° C., but then a somewhat longer period of heating is required. For example, two precipitates of magnesium ammonium phosphate which theoretically should have yielded residues weighing 0.2421 g each yielded 0.2420 and 0.2423 g, respectively, on ignition for three hours at 1,000° C. However, precipitates of twice this weight did not come to constant weight in five hours at the same temperature.

Table 2 shows the results of determinations of phosphorus in the standard solution of silver phosphate. The procedure just described was followed unless otherwise stated. The silver chloride which formed in the acid solution prior to the first precipitation dissolved when the solution was made ammoniacal, but a little of it may have remained. This was entirely eliminated in the second precipitation.

TABLE 2.—*Results obtained by precipitating phosphorus as* $MgNH_4PO_4 \cdot 6H_2O$ *and weighing as* $Mg_2P_2O_7$

[Final volume in all precipitations=150 ml]

	$Mg_2P_2O_7$		NH_4Cl present [1] (exclusive of that added through magnesia mixture)	NH_4OH (specific gravity 0.90) present
	Calculated	Found		
	g	*g*	*g*	*ml*
1	0.1876	0.1876	3.3	5
2	.1859	.1859	6.6	10
3	.1994	.1993	6.6	5
4	.3457	.3458	3.3	10
5	.0094	.0095	[2] 4–6	[2] 5–10
6	.0047	.0046	[2] 4–6	[2] 5–10
[3] 7	.2031	.2031	[2] 4–6	[2] 5–10
[3] 8	.1981	.1981	[2] 4–6	[2] 5–10
[4] 9	.2162	.2161	[2] 4–6	[2] 5–10
[4] 10	.1868	.1867	[2] 4–6	[2] 5–10
[5] 11	.2153	.2158	[2] 4–6	[2] 5–10
[5] 12	.2029	.2034	[2] 4–6	[2] 5–10

[1] This represents the ammonium chloride formed by the neutralization of the acid present in the solution.
[2] Between amounts given.
[3] Results obtained by applying the method to the filtrates and washings after precipitating the silver as chloride (Nos. 3 and 4 in Table 1).
[4] Results obtained by precipitating with molybdate reagent as is customary in rock analysis, dissolving the precipitate in NH_4OH, acidifying, and then applying the method as written.
[5] Silver was removed as in [4], but only 1 precipitation of magnesium ammonium phosphate was made.

The results in Table 2 were corrected for the solubility of magnesium ammonium phosphate and for the loss in weight of the platinum crucibles. The ignited precipitates were tested for silver and silica, but neither was found. No molybdenum was found in Nos. 9 and 10.

Gooch and Austin [14] and Epperson [15] have shown that large amounts of ammonium hydroxide or ammonium chloride are objectionable. The quantity of the latter can not always be controlled in the first precipation but is easily controlled in the second. The conditions outlined in the method can easily be met. In accurate work the second precipitation should be made because results by a single precipitation are usually high and can be correct only as a matter of chance, and then usually through compensating errors. In applied analyses the precipitation is not attempted until the phosphorus has been freed from other substances, such as arsenates or iron, that would also be precipitated. In applied analyses the positive errors obtained in single precipitations are usually more pronounced than is shown in Nos. 11 and 12 in Table 2.[16]

Directions which call for precipitations in hot [17] or neutral (pH about 7)[18] solutions are usually recommended as eliminating the

[14] See footnote 2, p. 280.
[15] See footnote 3, p. 280.
[16] For a discussion of single and double precipitations see The Analysis of Phosphate Rock, by G. E. F. Lundell and J. I. Hoffman, J. Assoc. Official Agri. Chem., **8**, p. 184; 1924.
[17] Gunner Jörgensen, The Analyst, **51**, No. 599, p. 61; 1926.
[18] Wolcott Gibbs, Am. J. Sci. (3), **5**, p. 114; 1873; and McCandless and Burton, Ind. Eng. Chem., **16**, p. 1267; 1924; **19**, p. 406; 1927.

necessity of a second precipitation. These shorter methods sometimes take as much of the analyst's time as is required by a second precipitation, and in the end the results are uncertain. For example, by the method of Jörgensen (single precipitation) in which the magnesia mixture is added dropwise to a hot ammoniacal solution of the phosphate and the solution then allowed to stand for four hours, 0.0806 and 0.0809 g of magnesium pyrophosphate were obtained from aliquot portions (50.00 ml each) of a solution of phosphoric acid. By applying the recommended procedure (double precipitation) described above, which has been shown to give the correct result, 0.0799 and 0.0798 g of magnesium pyrophosphate were obtained from similar aliquot portions. By using Jörgensen's method for the first precipitation and the recommended procedure for the second, excepting that in the second precipitation the solution was heated to boiling before the ammonium hydroxide was added, 0.0798 and 0.0798 g of magnesium pyrophosphate were obtained. In the last case the solution was cooled in ice water after the precipitate had settled, and it was then allowed to stand overnight.

(1) Solubility of Magnesium Ammonium Phosphate in the Determination of Phosphorus.—In order to determine the solubility of magnesium ammonium phosphate under the conditions of operation recommeded, ferric chloride (0.1 g) was added to the combined filtrates and washings from three determinations of phosphorus made by the recommended procedure. As each determination included two precipitations, the phosphorus represents that lost in six precipitations. The iron and phosphorus were precipitated with a slight excess of ammonium hydroxide, filtered, and the phosphorus then determined in a nitric-acid solution of the precipitate by adding molybdate reagent, filtering, washing, and titrating with alkali. Phosphorus equivalent to 0.0007 g of $Mg_2P_2O_7$ was found. This amounts to about 0.0001 g of $Mg_2P_2O_7$ for each precipitation and is significant only in determinations of such small amounts of phosphorus as are found in steels and similar materials.

(2) Ignition of Magnesium Ammonium Phosphate in the Determination of Phosphorus.—In most of the determinations of phosphorus that were made the crucibles containing the moist papers and precipitates were placed in a cold platinum wound electric muffle furnace. The current was then turned on and the temperature allowed to rise to 1,050° C. in the course of about two hours. In most cases ignition at 1,050° to 1,100° C. for one hour yielded residues that did not change in weight on further ignition in the same range, and in very few cases was it necessary to ignite for more than two hours at 1,050° to 1,100° C. to obtain constant weight. The residues were entirely free from carbon.

The use of temperatures above 1,100° C. is not advisable. W. F. Hillebrand[19] recommends a moderate blast giving a temperature less than 1,100° C. During the analysis of a phosphate rock one of the authors (H) obtained results for phosphorus which varied more than could be attributed to the ordinary sources of analytical errors. Méker, Fischer, and Tirrill burners had been used in the ignitions. As will be shown below, the variations may have been caused by losses in weight of either or both the crucibles or their contents.

[19] U. S. Geol. Surv. Bull., No. 700, p. 150.

In order to determine the maximum temperatures that could be obtained inside of a crucible by the use of these burners thermocouple wires were welded to the bottom on the inside of a platinum crucible, and the leads up the side of the crucible were insulated by surrounding them with silica tubes. The crucible was covered, and the burners were applied so as to give the maximum heat. The particular burners and gas tested (Washington, D. C., carbureted water gas) gave the following temperatures: Tirrill, 1,165° C.; Méker, 1,205° C.; Fischer, 1,240° C. The data given in Table 3 show that errors may result from prolonged ignition over any of the burners mentioned. A good blast lamp may give temperatures higher than 1,300° C. in a covered platinum crucible. A blast lamp should, therefore, never be used in the ignition of magnesium pyrophosphate unless it is certain that the temperature inside of the crucible can not exceed 1,100° C.

A platinum-wound electric muffle furnace with pyrometer is ideal for such ignitions, because the temperature can be controlled, the heat is evenly distributed throughout the crucible, and drafts and contaminations from gas burners are avoided. In many tests made by us none of the residues showed any visible carbon after ignition for one hour at 1,050° to 1,100° C. in the electric muffle furnace. Ignition at the full heat of a Tirrill or Fischer burner for as long as six hours often yields a residue which looks perfectly white on the surface and yet contains a black core. If ignitions are prolonged, the loss in weight of platinum crucibles must be taken into account.

The behavior of properly prepared pyrophosphates heated at different temperatures and the losses in weight of platinum-iridium crucibles are shown in Table 3. All of the temperatures of ignition reported in this and subsequent tables were measured with a platinum to platinum—10 per cent rhodium thermocouple connected to a high resistance millivoltmeter. This pyrometer was calibrated both before and after the investigation, the maximum difference between the two calibrations being 7° C. The furnace was explored for temperature differences, a maximum of 18° C. being found in the space used. The thermocouple was placed in an intermediate position. Taking into consideration the temperature differences in the furnace and the 10° C. accuracy certified for the pyrometer, it is believed that the temperatures of ignition reported are accurate within ±25° C. The empty crucible used as a blank was originally made from platinum containing 0.7 to 0.8 per cent of iridium. Emf measurements made by E. Wichers indicate that the composition was essentially the same at the time the experiments were made. The crucibles used in Nos. 2, 3, 4 and the blank were of the same lot, and all had been in use for at least 10 years. After dissolving the fused mass in the crucible used in No. 1, washing it out with water, igniting, and weighing, the crucible showed a loss of 0.0026 g as compared with its weight before the ignitions. The fused pyrophosphate, however, had attacked the platinum. By precipitating the platinum in the hydrochloric-acid solution of the fused mass with hydrogen sulphide and igniting the sulphide to metal, 0.0010 g of platinum was recovered. The loss through volatilization, therefore, was 0.0016 g.

TABLE 3.—*Ignition of $Mg_2P_2O_7$ in the determination of phosphorus*

	Duration and temperature of ignition (ignitions in sequence)	Weight of ignited residues				Weight of empty platinum crucible used as a blank	Remarks
		No. 1	No. 2	No. 3	No. 4		
		g	g	g	g	g	
1	Constant weight at 1,050° C.	0.1876	0.0094	0.2154	0.1982	27.0911	Ignited residue looked normal.
2	1 hour at 1,100° C.[1]	.1876	.0094	.2154	.1982	27.0911	Do.
3	1 hour additional at 1,100° C.	.1876	.0093	.2154	.1982	27.0910	Do.
4	1 hour at 1,150° C	.1876	.0092	.2151	.1979	27.0909	Do.
5	1 hour at 1,200° C	.1875	.0089	.2148	.1976	27.0907	Do.
6	1 hour at 1,250° C	.1873	.0084	.2143	.1974	27.0904	Ignited residue shrank.
7	1 hour at 1,300° C.[2]	.1859	.0069	.2131	.1953	27.0900	Ignited residue sintered.
8	1 hour at 1,400° C	.1800	.0062	.2085	.1898	27.0893	Ignited residue fused to a glass.
9	Theoretical weight of $Mg_2P_2O_7$ as calculated from Ag_3PO_4.	.1876	.0094	.2153	.1982		

[1] A precipitate, weighing 0.1859 g after ignition to constant weight at 1,050° C., was ignited for 3 hours at 1,100° C. and lost 0.2 mg. An empty platinum crucible ignited in the same way lost the same amount.
[2] A precipitate, weighing 0.3459 g after ignition to constant weight at 1,050° C., was ignited for 1 hour at 1,300° C. and lost 1.9 mg. The control crucible ignited in the same way lost 0.4 mg.

III. DETERMINATION OF MAGNESIUM

Gooch and Austin [20] have studied the effect of varying the concentrations of ammonium hydroxide and ammonium chloride during the precipitation of magnesium ammonium phosphate. They used a solution of magnesium nitrate which had been standardized by evaporating portions of the solution with sulphuric acid, igniting at a dull red heat, and weighing the magnesium as sulphate, $MgSO_4$. Epperson [21] used a solution of magnesium chloride which was standardized by evaporating measured portions with a suspension of mercuric oxide and then igniting to oxide.

1. PREPARATION OF A SOLUTION OF MAGNESIUM CHLORIDE

A solution of magnesium chloride was prepared by dissolving the purest available salt in dilute hydrochloric acid (1:500). The following tests for purity were made: No barium or strontium was found when sulphuric acid was added to a slightly acid (0.5 ml of HCl per 100 ml) solution of 5 g of the salt. No hydrogen sulphide metals were found in 5 g of the salt when hydrogen sulphide was passed into either the slightly acid or ammoniacal solution.

The following test for alkalies was applied: Ignite 2.0 g of the salt ($MgCl_2.6H_2O$) for one hour at about 600° C. to expel the water and most of the chloride, transfer the residue to an agate mortar, and mix thoroughly with 0.4 g of resublimed ammonium chloride and 4.0 g of calcium carbonate which has been especially prepared for the determination of alkalies. Determine alkalies by the usual J. Lawrence Smith method, but use a saturated solution of calcium hydroxide in washing the insoluble residue during the extraction of the sintered mass.[22] Blanks on the reagents must be carried through all

[20] F. A. Gooch and Martha Austin, Am. J. Sci., 4th series, **7**, p. 187; 1899; Chem. News, **79**, pp. 233 and 244; 1899; Z. anorg. Chem., **20**, p. 121; 1899.
[21] See footnote 3, p. 280.
[22] G. E. F. Lundell and H. B. Knowles, The Analysis of Soda Lime Glass, J. Am. Ceram. Soc., **10**, p. 822; 1927.

steps of the determination. The average weight of the alkali chlorides obtained in two determinations was 0.2 mg greater than the average weight obtained in two blanks.

As a matter of convenience tests for phosphorus and calcium were applied to the magnesium oxide obtained in the determination of magnesium by weighing as the oxide.

STANDARDIZATION OF THE SOLUTION OF MAGNESIUM CHLORIDE

The magnesium in the solution of magnesium chloride was determined by (*a*) weighing as the oxide, MgO, (*b*) weighing as the sulphate, $MgSO_4$, and (*c*) weighing as the pyrophosphate, $Mg_2P_2O_7$. The last is the method under observation, and its use is not strictly permissible as a part of the standardization. It is included here because of convenience of comparison. In Tables 4 to 7, inclusive, the results obtained by the first two methods are taken as the standard.

(a) DETERMINATION OF MAGNESIUM BY WEIGHING AS THE OXIDE

Weighed portions of the solution were evaporated in platinum crucibles with a suspension of mercuric oxide and then ignited to constant weight at 1,150° to 1,250° C. The treatment with mercuric oxide and the ignition were repeated until the weight checked the one obtained after the previous treatment. It is rather difficult to obtain constant weight. This is probably due, at least in part, to the occlusion of gases by magnesium oxide.[23] The ignited magnesia was tested for phosphorus by dissolving it in nitric acid and adding molybdate reagent. No phosphorus was found. Addition of silver nitrate to the nitric acid solution of one of the precipitates showed that no chloride was left in the ignited oxide. No calcium was found when one of the precipitates was dissolved in dilute sulphuric acid, and alcohol added so that the ratio of sulphuric acid: water alcohol was 1:9:90. Addition of barium chloride to the dilute hydrochloric acid solution of one of the ignited precipitates revealed no sulphate. No mercury was found in the ignited residue.

(b) DETERMINATION OF MAGNESIUM BY WEIGHING AS THE SULPHATE

Weighed portions of the solution of magnesium chloride were treated in a platinum crucible with 1 ml of sulphuric acid, evaporated to dryness in a radiator, and ignited to constant weight in a muffle at 700° to 750° C. The treatment with sulphuric acid and the ignition to constant weight were repeated. The results after the second treatment were the same as those after the first and did not change when the residues were treated with water, evaporated, and again ignited.

(c) DETERMINATION OF MAGNESIUM BY WEIGHING AS THE PYROPHOSPHATE (RECOMMENDED PROCEDURE)

The following procedure is recommended: To the nearly neutral solution containing 0.10 g or less of magnesia add 5 to 10 ml of hydrochloric acid, and adjust the volume of the solution to 125 to 150 ml.[24]

[23] T. W. Richards and E. F. Rogers, Am. Chem. J., **15**, p. 567; 1893; state that the oxide of magnesium retains on ignition sufficient occluded nitrogen and oxygen to increase the weight sensibly.

[24] In applied analyses salts may be in such concentration that they separate at this point, or subsequently when the solution is rendered ammoniacal. There is no objection in such analyses to making the first precipitation in a greater volume (250 to 400 ml); or the solution may be evaporated to dryness, the ammonium salts expelled by gentle ignition, and the residue dissolved in acid and water.

Cool the solution in ice water, add 10 ml of a freshly prepared solution of diammonium phosphate $(NH_4)_2HPO_4$ (25 g of the salt per 100 ml of water), then ammonium hydroxide slowly and with stirring until the solution is alkaline to litmus. Stir for a few minutes, then add 5 to 10 ml of ammonium hydroxide, and stir for a few minutes more. Allow the solution to stand for at least four hours, preferably overnight, then filter on a paper of close texture and wash with dilute ammonium hydroxide (1:19). Dissolve the precipitate in 50 ml of warm dilute hydrochloric acid (1:9), wash the paper thoroughly with hot dilute hydrochloric acid (1:99), dilute the solution to 125 to 150 ml, add ½ to 1 ml of the solution of diammonium phosphate, cool in ice water, and again precipitate the magnesium by the above procedure. Allow to stand for 4 to 24 hours, filter on a paper of close texture, and wash with dilute ammonium hydroxide (1:19) as before. Transfer the precipitate and paper to a weighed platinum crucible, char the paper without flaming, burn off the carbon at a temperature below 900° C., and finally ignite to constant weight, preferably in a muffle, at 1,100° C.[25] In applied analyses the precipitation of magnesium must, of course, follow the separation of other substances that would be precipitated in an ammoniacal solution containing phosphate.[26]

The results that were obtained by the three methods (*a*, *b*, and *c*) are given in Table 4. Because of the fact that there is a possibility of occluding gases in ignited magnesia, it is believed that in the standardization of the solution the result obtained by ignition as sulphate is to be preferred.

TABLE 4.—*Results obtained in the standardization of a solution of magnesium chloride*

(The results are given in terms of the weight of MgO per gram of solution)

	Weight of MgO found by—		
	Treating with HgO and weighing as MgO	Treating with H_2SO_4 and weighing as $MgSO_4$	Precipitating as $MgNH_4PO_4 \cdot 6H_2O$ and weighing as $Mg_2P_2O_7$ (method *c* above)
	g	*g*	*g*
1	0.005383	0.005380	0.005381
2	.005385	.005380	.005381
3	.005386	.005379	.005379
4			.005382
Averages	.005385	.005380	.005381

(1) SOLUBILITY OF MAGNESIUM AMMONIUM PHOSPHATE IN THE DETERMINATION OF MAGNESIUM.—It is difficult to make a direct determination of the solubility of magnesium ammonium phosphate under the conditions which obtain in the determination of magnesium,

[25] If precipitates are not too large (0.2 g or less) and have been obtained by the recommended procedure, satisfactory results can be obtained by igniting at 1,000° C., but then a longer period of heating is usually required. For example, the theoretical weight of pyrophosphate was obtained when precipitates yielding residues weighing 0.2055 and 0.1155 g were ignited for five hours at 1,000° C.

[26] Moderate amounts of certain elements, such as iron, chromium, titanium, zirconium, or tin need not be removed if ammonium citrate is added, Ind. Eng. Chem., **15**, pp. 44 and 171; 1923. Preliminary removals of calcium are usually incomplete. Any calcium that escapes will be precipitated together with magnesium.

but by the following indirect method it was shown that it is approximately the same as in the case of phosphorus:

By following the recommended procedure, but making five reprecipitations, 0.2542 g and 0.2687 g of $Mg_2P_2O_7$ were obtained, respectively, as compared with the theoretical values of 0.2545 g and 0.2690 g. The results were corrected for the loss in weight of the platinum crucibles. Thus, the results obtained by making a total of six precipitations were only 0.3 mg lower than the theoretical. The tests indicate that the equivalent of no more than 0.0001 g of $Mg_2P_2O_7$ is lost in each precipitation. While these results can not be regarded as conclusive, they are in accord with other experimental work by the authors.

(2) IGNITION OF MAGNESIUM AMMONIUM PHOSPHATE IN THE DETERMINATION OF MAGNESIUM.—The same precautions as to slow preliminary ignition, charring of paper, etc., which are necessary in the determination of phosphorus also hold in the determination of magnesium. The ignited precipitates gradually lose weight if they are heated at 1,200° C. or higher. Table 5 shows the results obtained in such ignitions.

TABLE 5.—*Ignition of magnesium ammonium phosphate to the pyrophosphate in the determination of MgO (double precipitation)*

(The precipitates were obtained by the recommended method (III, 2, *c*, p. 287))

No.	Time and temperature of ignition (ignitions in sequence)	Weights of precipitates [1]					Weight of empty platinum crucible [2] used as a blank	Remarks
		No. 1	No. 2	No. 3	No. 4	No. 5		
		g	*g*	*g*	*g*	*g*		
1	1 hour at 1,050° C	0.2765	0.4058	0.2190	0.4016	0.0887	18.8651	Ignited residues looked normal.
2	1 hour at 1,100° C	.2755	.4053	.2186	.4012	.0887	18.8649	Do.
3	1 hour additional at 1,100° C.	.2752	.4052	.2183	.4010	.0886	18.8648	Do.
4	do	.2749	.4051	.2183	.4006	.0885	18.8647	Do.
5	do	.2748	.4051	.2182	.4005	.0885	18.8646	Do.
6	do	.2748	.4050	.2182	.4003	.0884	18.8645	Do.
7	do	.2749	.4051	.2183	.4003	.0884	18.8644	Do.
8	do	.2749	.4050	.2183	.4001	.0884	18.8643	Do.
9	do	.2749	.4050	.2183	.4001	.0884	18.8642	Do.
10	1 hour at 1,150° C	.2749	[3]	.2183	[3]	0.883	18.8640	Do.
11	1 hour at 1,200° C	.2749	.4044	.2181	.3997	.0880	18.8638	Do.
12	1 hour at 1,250° C	.2747	.4040	.2181	.3993	.0877	18.8636	Ignited residues shrank.
13	1 hour at 1,300° C	.2744	[3]	.2174	[3]	.0871	18.8631	Ignited residues sintered.
14	Most probable weight of $Mg_2P_2O_7$ as calculated from weight of standard solution taken.	.2748	.4046	.2182	.3996	.0884		

[1] These results represent the weights of the precipitates of $Mg_2P_2O_7$, corrected for the loss in weight of the platinum crucibles. At the end of the ignitions the precipitates were brushed out and the empty crucibles weighed. The crucible used for precipitate No. 1 lost 0.0018 g, that for No. 3 lost 0.0016 g, and that for No. 5 lost 0.0018 g as compared with a loss of 0.0020 g in the case of the empty crucible used as a blank. These differences in the losses are insignificant when they are distributed over 13 ignitions.

[2] This crucible was made of platinum containing about 1.2 per cent of iridium. The crucibles used in the other experiments in this table were of the same lot and had been in use for 5 years. Emf. measurements made by E. Wichers indicate that the present iridium content is about the same as it was originally.

[3] Omitted.

The first result is that obtained by slowly igniting in a muffle and then holding the temperature at 1,050° C. for one hour. The duration and temperature of the subsequent ignitions are those shown in the table.

The data in Table 5 show the following points: (1) Magnesium pyrophosphate obtained in the determination of magnesium by the

recommended procedure does not lose weight upon prolonged ign tion at 1,100° C. This point is further illustrated in Table 7. (2) ignitions are prolonged, corrections should be made for the loss weight of platinum crucibles.[27] (3) At about 1,200° C. the resid begins to lose weight. The rate of loss increases with increase temperature. (4) Precipitates yielding 0.3 g or less of pyropho phate are more readily ignited to constant weight than larger ones.

An inspection of Table 6 shows that precipitates formed in th presence of a large excess of phosphate require a longer time for ign tion to constant weight at temperatures below 1,100° C. than required in the case of those formed in the presence of 0.25 g of diam monium phosphate (the maximum prescribed in the recommende procedure). The positive error is greatest in the case of large pr cipitates. The weights of the precipitates are corrected for th losses in weight of the platinum crucibles. Excess precipitant ha been shown to yield high results in the determination of phosphorus although there is no particular difficulty in igniting precipitates s obtained to constant weight.

These results emphasize the necessity of making two precipitation and of carefully avoiding a large excess of phosphate in the second The addition of one-half to 1 ml (equivalent to 0.12 to 0.25 g of th salt) of the solution of diammonium phosphate in the second pr cipitation is ample. If two precipitations are not made, there i no convenient way of determining this excess. In Table 6 the result which were obtained by the use of a large excess of phosphate ar more accurate than could be expected by a single precipitation i applied analyses, for in the latter the solutions may contain an accu mulation of salts that give rise to contamination by compounds such as $MgNaPO_4$.

The determinations on which Table 7 is based were made in orde to compare the behavior on ignition of precipitates of magnesium ammonium phosphate obtained in the determination of phosphorus with those obtained in the determination of magnesium.

The precipitations were made by the recommended methods de scribed above, and the ignitions were made as indicated in the table During all ignitions the crucibles were placed in the furnace so that they all received essentially the same treatment. Two series o determinations were made. Those in columns 3, 4, 7, and 8 were made about two months after the others. The results are corrected for loss in weight of the platinum crucibles. The total loss in weight of the platinum crucible used as a blank with Nos. 3 and 4 was 0.0035 g. The loss in weight of the crucible used as a blank with Nos. 7 and 8 was also 0.0035 g. As this represents a total period of ignition of 40 hours between 1,050° and 1,200° C., it shows that a loss of a little less than 0.1 mg per hour is to be expected if the ignition is made in a muffle furnace.[29]

---

[27] Heating in a muffle at 1,100° C. caused an average loss in weight of about 0.1 mg per hour, but it is not safe to use this correction in all cases, because different crucibles may not show the same losses. Ignition over the full heat of a Fischer burner (maximum 1,240° C. with the gas used) caused a loss of only 0.3 mg in 18 hours in the case of an empty crucible used as a control. After this heating the same crucible showed a loss of 0.6 mg in 4 hours in the muffle at 1,100° C. The empty crucible used to obtain the data in Table 6 when heated for 26 hours at the maxiumm heat of a Fischer burner lost only 0.4 mg, but subsequent heating in a muffle at 1,100° C. caused a loss in weight of 0.4 mg in 4 hours.

[28] J. Assoc. Official Agri. Chem., 8, p. 184; 1924.

[29] In these experiments platinum-iridium crucibles (about 0.4 per cent of Ir) were used side by side with platinum-rhodium crucibles (about 3.5 per cent of Rh), and the behavior of both with respect to loss of weight was about the same. In fact, the empty crucibles used as blanks, one of which was made of platinum-iridium and the other of platinum-rhodium, showed exactly the same loss in weight.

[Final volume in all precipitations=150 ml]

No.	Time and temperature of ignition (ignitions in sequence)	$MgNH_4PO_4 \cdot 6H_2O$ obtained by double precipitation									Weight of empty platinum crucible used as a blank	Remarks
		(0.25 g $(NH_4)_2HPO_4$ present in second precipitation.) Weight of $Mg_2P_2O_7$			(1.5 g $(NH_4)_2HPO_4$ in excess.) Weight of $Mg_2P_2O_7$			(3.0 g $(NH_4)_2HPO_4$ in excess.) Weight of $Mg_2P_2O_7$				
		No. 1	No. 2	No. 3	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3		
		g	g	g	g	g	g	g	g	g	g	
1	1 hour at 1,050° C	0.1093	0.2357	0.4422	0.1250	0.2454	0.5088	0.1033	0.2561	0.3891	27.0340	Ignited residues were white and appeared normal.
2	1 hour additional at 1,050° C	.1090	.2348	.4416	.1247	.2451	.5072	.1031	.2556	.3877	27.0338	Do.
3	do	.1091	.2345	.4414	.1248	.2444	.5060	.1030	.2553	.3864	27.0337	Do.
4	do	.1090	.2341	.4415	.1248	.2442	.5048	.1031	.2552	.3857	27.0337	Do.
5	do	.1090	.2339	.4412	.1248	.2439	.5033	.1030	.2547	.3843	27.0337	Do.
6	do	.1090	.2339	.4413	.1248	.2438	.5020	.1029	.2545	.3830	27.0336	Do.
7	do	.1090	.2339	.4412	.1248	.2436	.5007	.1028	.2542	.3822	27.0336	Do.
8	do	.1090	.2339	.4412	.1247	.2435	.5002	.1028	.2539	.3817	27.0335	Do.
9	1 hour at 1,100° C	.1089	.2339	.4412	.1247	.2435	.5000	.1026	.2538	.3814	27.0334	Do.
10	1 hour at 1,200° C	-------	.2334	.4409	-------	.2433	.4996	-------	.2534	.3807	27.0333	Ignited residues shrank.
11	1 hour at 1,300° C	-------	.2321	.4394	-------	.2424	.4988	-------	.2526	.3799	27.0332	Ignited residues sintered
12	1 hour at 1,400° C	-------	.2289	.4347	-------	.2400	.4906	-------	.2500	.3737	27.0327	Ignited residues fused.
13	Most probable weight of $Mg_2P_2O_7$ as calculated from weight of standard solution taken.	.1090	.2338	.4412	.1248	.2436	.4991	.1027	.2539	.3801	----------	

TABLE 7.—*Comparative ignitions of precipitates obtained in determinations magnesium and of phosphorus by the recommended procedures*

No.	Duration and temperature of ignitions (ignitions in sequence)	Weight of $Mg_2P_2O_7$ obtained in the determination of magnesium				Weight of $Mg_2P_2O_7$ obtained the determination of phosph			
		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No.
		g	*g*	*g*	*g*	*g*	*g*	*g*	*g*
1	1 hour at 1,050° C	0.2585	0.2694	0.2554	0.2708	0.2896	0.2881	0.4854	0.
2	1 hour additional at 1,050° C	.2583	.2689	.2548	.2695	.2895	.2881	.4847	
3	do	.2575	.2682	.2548	.2696	.2894	.2880	.4847	
4	1 hour at 1,100° C	.2568	.2673	.2547	.2693	.2892	.2880	.4846	
5	1 hour additional at 1,100° C	.2568	.2671	.2546	.2692	.2892	.2880	.4846	
6	do	.2568	.2671	.2546	.2692	.2892	.2881	.4846	
7	do	.2566	.2672	.2546	.2691	.2892	.2881	.4846	
8	do	.2566	.2672	.2546	.2691	.2892	.2881	.4846	
9	do	.2566	.2672	.2545	.2692	.2892	.2881	.4845	
10	do	.2566	.2672	.2546	.2692	.2892	.2881	.4845	
11	do	.2566	.2672	.2546	.2691	.2892	.2881	.4846	
12	do	.2565	.2672	.2545	.2691	.2892	.2881	.4846	
13	5 hours additional at 1,100° C	.2566	.2673	.2546	.2692	.2892	.2881	.4846	
14	1 hour at 1,200° C	.2565	.2671	.2541	.2689	.2890	.2880	.4843	
15	1 hour additional at 1,200° C	.2564	.2668	.2540	.2688	.2889	.2879	.4843	
16	do	.2563	.2666	.2540	.2688	.2888	.2878	.4841	
17	do			.2538	.2687			.4838	
18	do			.2538	.2687			.4837	
19	do			.2537	.2686			.4837	
20	do			.2537	.2686			.4836	
21	do			.2536	.2686			.4836	
22	do			.2535	.2684			.4835	
23	5 hours additional at 1,200° C			.2531	.2682			.4831	
24	10 hours additional at 1,200° C			.2527	.2679			.4829	
25	Most probable weight of $Mg_2P_2O_7$	.2567	.2672	.2546	.2691	.2893	.2881	.4847	

The data given in Table 7 show that after constant weight reached the pyrophosphate residues obtained in the determination magnesium and phosphorus behave similarly upon further ignitio The data also show that constant weight is reached more quickly the determination of phosphorus than in the determination of ma nesium. However, after constant weight was once obtained t results did not change in either case upon prolonged ignition 1,100° C. There is a very slow but definite loss in weight if t residues are ignited at 1,200° C. Residues obtained by gradual heating precipitates to 900° C. until the carbon was burned off a then heating immediately for periods of one hour at 1,200° C showed a behavior upon further ignition at 1,200° C. similar to th of precipitates which received the prolonged intervening ignition 1,100° C. shown in Table 7.

The longer time required for the satisfactory ignition of the pr cipitate obtained in the determination of magnesium is probably result of the formation of a compound containing an excess of pho phate, such as $Mg(NH_4)_4(PO_4)_2$. Upon ignition of this compoun magnesium metaphosphate, $Mg(PO_3)_2$, is formed which causes t result to be slightly high. Longer ignition or ignition at a high temperature probably converts this compound to the pyrophospha as follows: $2Mg(PO_3)_2 = Mg_2P_2O_7 + P_2O_5$. A large excess of dia monium phosphate will cause the formation of more of the compoun rich in phosphorus and probably accounts for the long period ignition required in the case of some of the residues in Table 6.

Table 7 also shows that if ignition is prolonged at 1,100° C. co rection must be made for the loss in weight of the platinum crucible

It is worthy of note that the loss in weight of the crucibles during 24 hours of heating at 1,200° C. was slightly greater than the net loss in weight of the pyrophosphate residues. This means that if the loss in weight of the crucibles had been neglected, the total loss in weight would have been attributed to the pyrophosphate residues and would have been more than twice as great as it was actually shown to be.

IV. SUMMARY

The conditions necessary for obtaining a final product that has the formula $Mg_2P_2O_7$ in determinations of phosphorus or magnesium are set forth. These conditions were tested by applying the methods as written to carefully prepared standards of reference.

The solubility of magnesium ammonium phosphate in the procedure recommended for the determination of phosphorus is equivalent to approximately 0.0001 g of $Mg_2P_2O_7$ for each precipitation, including the attendant washing. There is no evidence that it is greater in the determination of magnesium.

The temperature at which magnesium pyrophosphate is ignited deserves more attention than it has received in the past. Ignition to constant weight at 1,100° C. is recommended in accurate work. At 1,000° C. constant weight is obtained slowly, particularly with large residues while at 1,200° C. there is a slow but definite loss in weight. It is more difficult to obtain constant weight in determinations of magnesium than in determinations of phosphorus.

Prolonged ignition in a muffle at temperatures above 1,000° C. causes appreciable losses in weight of platinum crucibles. It is shown that it is necessary to make corrections for these losses.

The temperatures that can be obtained with three types of burners are given.

WASHINGTON, March 7, 1930.

NEW DESIGN OF PRECISION RESISTANCE STANDARD

By James L. Thomas

ABSTRACT

As a result of investigations of the causes of the slight changes in the resistance standards of the type developed by Josa, a new type of precision resistance standard has been developed. The coils are wound of bare manganin wire and annealed at a red heat in order to remove the winding strains. They are mounted in double-walled sealed containers which contain no oil or other cooling liquid. A group of new 1 ohm coils, for which data are given, have been remarkably constant in resistance.

CONTENTS

	Page
I. Introduction	295
II. A new method of annealing	296
III. Data on new standards	296
1. One ohm No. 42	297
2. One ohm No. 36	297
3. One ohm No. 38	298
4. One ohm coil, not numbered	298
5. One ohm No. 46	299
6. One ohm No. 47	299
7. One ohm No. 48	299
8. One ohm No. 49	300
9. One ohm No. 52	300
IV. Discussion of data	300
1. Material	300
2. Annealing	301
3. Stability	301
4. Temperature coefficient	302
V. Design of container	302
VI. Summary	304
VII. Acknowledgments	304

I. INTRODUCTION

Since 1910 the unit of electrical resistance for this country has been maintained by 1 ohm standards of the type developed by Rosa and described by him in a bulletin of this bureau.[1] A number of these 1 ohm standards are kept under observation, and it is assumed that the average resistance of the 10 best standards in this group remains constant. The individual standards of this reference group of 10 seldom show changes greater than 3 or 4 parts in 1,000,000 per year with respect to the average. If an unusually large change is shown by one of the standards, it is discarded from the group of 10 and replaced by one which has shown a satisfactory performance in the preceding several years.

The unit of resistance which has been so maintained has probably not changed on the average by more than 1 part in 1,000,000 per year since 1910, although there are indications that this average yearly change may be increasing. Moreover, the increasing accu-

[1] B. S. Bull., 5, p. 413; 1908.

racy with which electrical measurements are being made has made seem desirable to still further increase the stability of standards us for this purpose. With this in mind, experiments were begun 1928 at this bureau to ascertain the causes of the small changes the resistance of standards of the sealed type.

While no complete explanation of the changes in resistance h been found, a new design of 1 ohm standard has been developed as result of these investigations. Several standards of this new ty have been under observation for over a year, and their performan to date leads to the expectation that they will prove far superior those now in use. This increase in stability has apparently result from the removal of the winding strains by annealing the resistan coils at a red heat, from the use of a better quality of manganin wi and from the use of a new design of sealed container.

II. A NEW METHOD OF ANNEALING [2]

Coils for the standards designed by Rosa were prepared and bak according to the methods used at the Physikalisch-Technisc Reichsanstalt and described by Feussner [3] and Lindeck.[4] Sil covered manganin wire was wound on silk-covered brass tub impregnated with shellac varnish, and baked for several hours in at 140° C., the maximum temperature to which the silk insulati could safely be subjected. This baking reduced the resistance of t coils, probably as the result of a partial annealing, and increased t stability of their resistance. During the first few weeks after such annealing, however, there is a rise in resistance of the coils amounti to 0.01 per cent or more in many cases. For this reason the bak coils are generally kept several months before they are used.

Since baking at 140° C. removed to only a limited extent the strai produced in the wire during manufacture and those resulting fro winding, it was decided to try a higher temperature in order to anne the wire more thoroughly. To do this, several coils of bare mangani wire were wound on mandrels and properly spaced with bare copp wire. They were then placed in a vacuum Arsem furnace and heate to a temperature of 500° C. or above. This so thoroughly anneale the coils that they held their shapes perfectly upon removal from t mandrels. They were then slipped onto silk-insulated brass tub of the same diameter as that of the mandrels, tied down and space with linen thread, shellacked and baked for an hour at about 80° Several temperatures and times of annealing were tried, the be results being obtained when the furnace temperature was raise slowly to about 550° C., and the furnace then allowed to cool wit the power cut off.

III. DATA ON NEW STANDARDS

The following tables show the performance of a number of 1-oh standards whose coils were annealed at a red heat. They include s coils which have so far been annealed by the method which w decided upon as most satisfactory. The resistances are expressed i

[2] After this paper had been written the attention of the author was called to the fact that Burstall, 1896, annealed the coils for a resistance box at red heat by passing a current through them. Phil. Ma **42**, fifth series, p. 210; 1896.

[3] Zeitschr. für Instrumentk., **10**, p. 6; 1890.

[4] British Association Report, p. 145; 1892.

rms of the "International Ohm" maintained, as explained above, nce 1910 at the National Bureau of Standards by means of wire-ound resistance standards. This unit is the so-called Washington nit.[5] The values of α and β listed under the heading of "tempera-re coefficient" are defined by the equation

$$R_t = R_{25}[1 + \alpha\ (t-25) + \beta(t-25)^2]$$

here R_t is the resistance at $t°$ C. and R_{25} is the resistance at 25° C.

1. ONE OHM NO. 42

Material.—No. 16 AWG (0.051 inch = 1.29 mm) manganin wire btained from the Driver-Harris Co., Harrison, N. J. Chemical nalysis of sample taken from same spool: Copper 81.7 per cent, anganese 11.8 per cent, nickel 5.1 per cent, iron 1.4 per cent.

Thermoelectromotive force.—Against copper, in interval 20°–30° C., hermal electromotive force is 1.8 microvolts per ° C. for the unan-ealed wire.

Annealing.—Annealed July 14, 1928, in Arsem furnace for 20 inutes at about 600° C.

Resistance.—

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1928		1928	
July 17	0.999928	Nov. 30	0.999931
Aug. 13	.999932	Dec. 10	.999931
Aug. 21	.999931	Dec. 22	.999931
Aug. 25	.999930	1929	
Sept. 1	.999932	Jan. 18	.999932
Sept. 5	.999931	Jan. 28	.999932
Sept. 13	.999931		
Sept. 24	.999931	Feb. 27	.999932
Oct. 4	.999930	Mar. 16	.999932
		Apr. 2	.999931
Oct. 22	.999931	May 8	.999932
Nov. 4	.999931		
Nov. 14	.999931	July 22	.999933
Nov. 26	.999931	Oct. 2	.999931

Temperature coefficient.—For finished coil in the interval 20° to 30° C. $\alpha = 19.4 \times 10^{-6}$, $\beta = -0.22 \times 10^{-6}$. For sample of wire from same spool, without annealing, $\alpha = -0.9 \times 10^{-6}$, $\beta = -0.42 \times 10^{-6}$.

2. ONE OHM NO. 36

Material.—No. 14 AWG (0.064 inch = 1.63 mm) manganin wire, obtained from the Driver-Harris Co., Harrison, N. J. Chemical analysis of sample taken from same spool: Copper 79.1 per cent, manganese 10.2 per cent, nickel 10.3 per cent, iron 0.4 per cent.

Thermoelectromotive force.—Against copper, in interval 20° to 30° C., thermal electromotive force is 4.3 microvolts per ° C. for unannealed wire.

Annealing.—Arsem furnace was slowly brought up to about 550° C. and then allowed to cool with pump in operation. Annealed October 1, 1928.

Resistance.—

[5] See Report to the International Committee on Electrical Units and Standards, Jan. 1, 1912, published by this bureau.

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1928		1929	
Oct. 4	1.000038	Jan. 12	1.000038
Oct. 6	1.000038	Jan. 28	1.000038
Oct. 22	1.000038	Feb. 11	1.000038
Oct. 27	1.000038	Feb. 27	1.000039
Nov. 5	1.000038	Mar. 16	1.000039
Nov. 10	1.000038	Apr. 2	1.000037
Nov. 16	1.000038	May 8	1.000038
Nov. 19	1.000038	May 25	1.000038
			1.000038
Nov. 26	1.000038	June 3	1.000038
Nov. 30	1.000038	June 20	1.000038
Dec. 10	1.000038	Nov. 12	
Dec. 22	1.000038		

Temperature coefficient.—For the completed coil in the interval 20° to 30° C. $\alpha = 12.5 \times 10^{-6}$, $\beta = -0.18 \times 10^{-6}$. For sample of wire taken from same spool and measured without annealing, in the same interval, $\alpha = 6.7 \times 10^{-6}$, $\beta = -0.3 \times 10^{-6}$.

3. ONE OHM NO. 38

Material.—Same as for No. 36.
Annealing.—Same as for No. 36. Annealed November 9, 1928.
Resistance.—

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1928		1929	
Nov. 10	0.999981	Jan. 12	0.999978
Nov. 12	.999981	Jan. 28	.999978
Nov. 14	.999981	Feb. 27	.999978
Nov. 16	.999980	Mar. 16	.999978
Nov. 19	.999980	Apr. 2	.999977
Nov. 22	.999979	May 8	.999977
Nov. 26	.999979	May 25	.999977
Nov. 30	.999979	June 1	.999977
Dec. 10	.999979	June 20	.999977
Dec. 26	.999979	Nov. 12	.999977

Temperature coefficient.—For completed coil in the interval 20° to 30° C. $\alpha = 11.6 \times 10^{-6}$, $\beta = -0.22 \times 10^{-6}$.

4. ONE-OHM COIL, NOT NUMBERED

Material.—Same as for No. 36.
Annealing.—Same as for No. 36. Annealed December 18, 1928.
Resistance.—

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1928		1929	
Dec. 22	0.999509	Jan. 28	0.999523
Dec. 26	.999515	Feb. 11	.999524
Dec. 28	.999516	Feb. 27	.999525
		Mar. 16	.999526
1929		Apr. 2	.999526
Jan. 7	.999519	May 8	.999529
Jan. 12	.999520	June 3	.999530
Jan. 18	.999521		

Temperature coefficient.—For completed coil in the interval 20° to 30° C. $\alpha = 14.6 \times 10^{-6}$, $\beta = -0.28 \times 10^{-6}$.

Remarks.—This coil was damaged when the copper terminal plates were silver soldered to the ends of the coil. After this soldering there was a fairly large area where the wire appeared to have been blistered. This area was cleaned with emery cloth and the coil was mounted in order to see what effect the overheating would produce. This probably accounts for the instablity of the resistance and for the slightly larger temperature coefficient.

5. ONE OHM NO. 46

Material.—From same spool as No. 36.

Annealing.—Same as for No. 36. Annealed May 17, 1929.

Resistance.—

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1929		1929	
June 3	0.999499	July 10	0.999503
June 4	.999501	July 22	.999503
June 10	.999502	Aug. 14	.999503
June 12	.999501	Aug. 28	.999503
June 19	.999502	Oct. 2	.999502
June 25	.999502	Nov. 9	.999502
June 28	.999503		

Temperature coefficient.—For completed coil in the interval 20° to 30° C., $\alpha = 10.9 \times 10^{-6}$, $\beta = -0.19 \times 10^{-6}$.

6. ONE OHM NO. 47

Material.—From same spool as No. 36.

Annealing.—Same as for No. 36. Annealed May 28, 1929.

Resistance.—

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1929		1929	
June 3	0.999490	July 10	0.999490
June 4	.999491	July 22	.999490
June 10	.999490	Aug. 6	.999490
June 12	.999490	Aug. 14	.999490
June 19	.999490	Aug. 28	.999490
June 25	.999490	Oct. 2	.999487
June 28	.999490	Nov. 9	.999487

Temperature coefficient.—For completed coil in the interval 20° to 30°C., $\alpha = 11.7 \times 10^{-6}$, $\beta = -0.15 \times 10^{-6}$.

7. ONE OHM NO. 48

Material.—From same spool as No. 36.

Annealing.—Same as for No. 36. Annealed May 22, 1929.

Resistance.—

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1929		1929	
June 10	0.999508	July 22	.0999511
June 12	.999509	Aug. 6	.999512
June 19	.999509	Aug. 14	.999512
June 25	.999510	Aug. 28	.999512
June 28	.999510	Oct. 2	.999510
July 10	.999511	Nov. 9	.999511

Temperature coefficient.—For completed coil in the interval 20° 30° C., $\alpha = 12.7 \times 10^{-6}$, $\beta = -0.32 \times 10^{-6}$.

8. ONE OHM NO. 49

Material.—From same spool as No. 36. Before annealing this c was plated with a thin coating of gold. Plated June 11, 1929.

Annealing.—Same as for No. 36. Annealed June 19, 1929.

Resistance.—

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1929		1929	
June 24	0.999490	Aug. 6	0.999492
June 25	.999490	Aug. 14	.999492
June 28	.999491	Aug. 28	.999492
July 10	.999492	Oct. 2	.999491
July 22	.999491	Nov. 9	.999491
July 29	.999491		

Temperature coefficient.—For completed coil in the interval 2° 30° C., $\alpha = 12.4 \times 10^{-6}$; $\beta = -0.24 \times 10^{-6}$.

9. ONE OHM No. 52

Material.—No. 14 AWG (0.064 inch = 1.63 mm) manganin w obtained from the Driver-Harris Co., Harrison, N. J., in August, 192 Chemical analysis of sample taken from same spool: Copper, 82.9, p cent; manganese, 12.6 per cent; nickel, 4.1 per cent; iron less th 0.3 per cent.

Thermoelectromotive force.—Against copper, in the interval 20° 30° C., thermal electromotive force is 1.2 microvolts per °C. for t unannealed wire.

Annealing.—Same as for coil No. 36. Annealed August 20, 192

Resistance.—

Date	Resistance at 25° C.	Date	Resistance at 25° C.
1929		1929	
Aug. 22	0.999528	Oct. 2	0.999527
Aug. 23	.999527	Oct. 23	.999528
Aug. 28	.999527	Nov. 2	.999528
Sept. 18	.999528		

Temperature coefficient.—For completed coil in the interval 20° 30° C., $\alpha = 6.1 \times 10^{-6}$; $\beta = -0.5 \times 10^{-6}$. For sample of wire taken fr same spool, without annealing, $\alpha = -3.3 \times 10^{-6}$; $\beta = -0.5 \times 10^{-6}$.

IV. DISCUSSION OF DATA

1. MATERIAL

These 1-ohm standards were made from three lots of wire whi differed greatly in composition. For example, No. 36 had about per cent more nickel but 2 per cent less manganese than coil No. 5 In spite of this wide difference in composition, the coils have remained very constant in resistance. This seems to indicate th

tle improvement in stability can be expected as a result of careful ntrol of the composition of the manganin.

The wire used in making these coils appeared to have been very refully handled during fabrication, showing no evidence of surface acks. Before winding, the wire was very carefully polished with a ne grade of emery paper and then cleaned with alcohol, as it is tirely possible that the condition of the surface of the wire has nsiderable influence upon the stability.

2. ANNEALING

The annealing given coil No. 36 was found most satisfactory. hen annealed at an appreciably lower temperature the coils would pand upon removal from the mandrels, thus showing that the nding strains had not been thoroughly removed. When annealed r a long time at 550° C., or at a higher temperature, the coils were ss constant in resistance, suggesting an undue amount of surface tion.

As yet, no attempt has been made to ascertain the nature of the rface action which takes place during the annealing. The atmos- here in the furnace is probably carbon monoxide gas at a pressure 2 or 3 mm of mercury. After annealing in this atmosphere, the ils are grayish brown in color. Even coil No. 49, which had eviously been gold plated, showed considerable discoloring of the rface as a result of the annealing.

3. STABILITY

It is obvious that these new 1-ohm standards have remained markedly constant in resistance, as compared with new coils made cording to the usual practice. Some of the standards have shown o appreciable change, while the remainder, except for one damaged soldering, changed in resistance by 3 or 4 parts in 1,000,000, nerally during the first month, with little or no change thereafter. is possible that this initial change is due to a slight burning of the anganin wire where terminal plates are silver soldered to the ends. he standards with which these new ones were compared were meas- red every six months in terms of the reference group of 10. At each easurement they were found to have changed slightly in resistance, nd hence it is possible that the new standards would have appeared ven more constant in resistance than appears from the data had ey been measured each time in terms of the reference group.

Since 1-ohm coils annealed at 550° C. proved to be very stable in sistance, the same annealing was tried for coils of other values. hese, however, have not been very satisfactory, especially the coils small wire. If the method is to be used, it seems probable that a ifferent heat treatment will be required for each size of wire.

In making international comparisons of resistance standards, con- iderable uncertainty has been introduced by changes that take ace during shipment. Some experiments with the effect of temper- ture upon the constancy of resistance standards point to heating as possible cause of this change in resistance. Three of the Rosa ype of sealed standards were put in an oven and maintained at 35° C. or a week, after which the temperature was raised to 45° C. and he standards maintained at that temperature for an additional week.

At the end of the two weeks, one standard had decreased in resistance by 9 parts in 1,000,000 while the other two had increased by 5 and 1 parts, respectively. Two of the new standards were given the same treatment and showed no change. Three of the new standards were therefore sent to Europe during the summer of 1929 for measurement in the British and German national laboratories. These were sent in June and received back in November. Measurements before sending and upon their return gave the same values to the nearest part in a million. It should be stated, however, that these standards were carried by hand instead of being shipped by express. For this reason there was no chance of their being subjected to temperatures as high as would be possible if carried in the hold of a steamship. However, since they showed no change when kept at a temperature of 45° C. for a week, it is not believed that any temperature encountered during shipment would appreciably alter their resistance.

4. TEMPERATURE COEFFICIENT

Of the standards for which data are given, seven were made from the same spool of manganin wire. Except for the rejected coil, the spread in the values of α for these standards is about 2 parts in 1,000,000, the values being five or six millionths higher than for the wire from which the coils were wound. The increase is due primarily to the baking, as the resistance of the copper terminal plates is such as to raise the temperature coefficient by just about 1 part in 1,000,000. This latter increase could be avoided by using manganin terminal plates. In view of the small spread in the values of α for the completed standards, it appears quite feasable to start with wire having the proper negative value of α and obtain completed standards with extremely small temperature coefficients.

V. DESIGN OF CONTAINER

A number of the standards made according to Rosa's design have developed slight leaks around the terminals where they pass through the hard-rubber tops, thus reducing the advantage obtained by sealing the standards. When opened, the oil in these containers was found to be acid, although it is not known whether or not this is due to their becoming unsealed. In order to avoid the chance of the resistance being affected by anything in the oil, the new standards have been mounted in double-walled containers which contain no oil or other cooling liquid. Double-walled containers used at this bureau for a number of years to seal coils for use in bridges have proved quite satisfactory, and they were readily adapted for use as cases for standards.

The containers are made of two coaxial brass tubes differing only slightly in diameter. These tubes are held apart at each end by metal rings, and the space between the tubes is sealed by soldering the rings to the tubes. The inside tube, shown in Figure 1 (*a*), is 6 cm in diameter and a half millimeter thick. One end of this tube is spun outward to form a flange of the same diameter as the inside of the larger tube, which is 7 cm in diameter and also a half millimeter in thickness. A short piece of thin brass tubing, which telescopes with the latter is spun inward to form a flange and then soldered into the upper end of the 7-cm tube, as shown in Figure 1 (*b*). The two

halves of the container are then assembled and soldered to form the completed container shown in Figure 1 (*c*). The walls of the container are very thin; and if tinned in advance, the two parts may be soldered together without unduly heating the coil, which occupies the closed space between the tubes.

The success of this type of container is due to the method of sealing the leads which was devised by Wenner and described in a paper by Waidner, Dickinson, Mueller, and Harper.[6] The leads are brought through holes drilled through the inner container wall. These holes are covered with copper plates, bent to fit snugly against the container wall. The coil ends are silver soldered to these plates. At the center of the plates are silver-soldered braided copper lead wires, as shown in Figure 2. A layer of silk cloth impregnated with gum shellac is placed between the copper plates and the container wall; the shellac is melted by applying a hot soldering copper to the copper plate and then the plate is pressed down tightly against the container wall, covering the holes, with the flexible lead wires passing through.

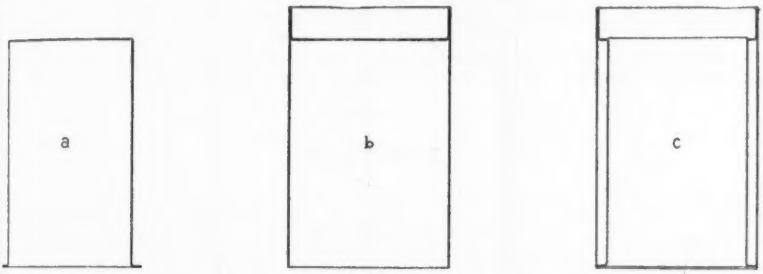


FIGURE 1.—*Cross section of container for new type of resistance standards*

When the shellac cools and hardens, a tight seal is obtained with good insulation for the leads.

After the coils have been annealed on a 6-cm mandrel, they are cut to the desired length and the copper plates are silver soldered to their ends, care being taken not to heat the wire unnecessarily. The coils are then slipped over the silk-covered inner tubes of the containers in such a way as not to make any permanent bends in the wire. After sealing the leads, the coils are pulled down tightly against the container wall, tied, and spaced with linen thread, after which they are shellacked and baked at 80° C. Final adjustment of the resistance is then made by carefully filing in such a way that no filings get down between the turns of the coil. The filed part is then shellacked and allowed to air dry, or is it again baked at 80° C. After final adjustment, the containers are assembled and soldered, the leads then being soldered to the proper terminals, which are mounted in a hard-rubber or bakelite top. A view of the completed standard is shown in Figure 2. Although no liquid is put in the container the construction is such as to give very effective cooling, especially when kept in a well-stirred oil bath. The standards assume the temperature of the bath much more rapidly than do those of the Rosa type.

[6] B. S. Bull., **11**, p. 575; 1915.

VI. SUMMARY

1. Precision resistance standards of the type developed by Ros undergo changes in resistance.

2. By annealing the resistance coils at a red heat, the constancy o 1-ohm resistance coils has apparently been greatly increased, the bes results being obtained from coils annealed at about 550° C.

3. The average change in resistance of 1-ohm coils that have bee under observation for as much as six months is slightly over 2 par

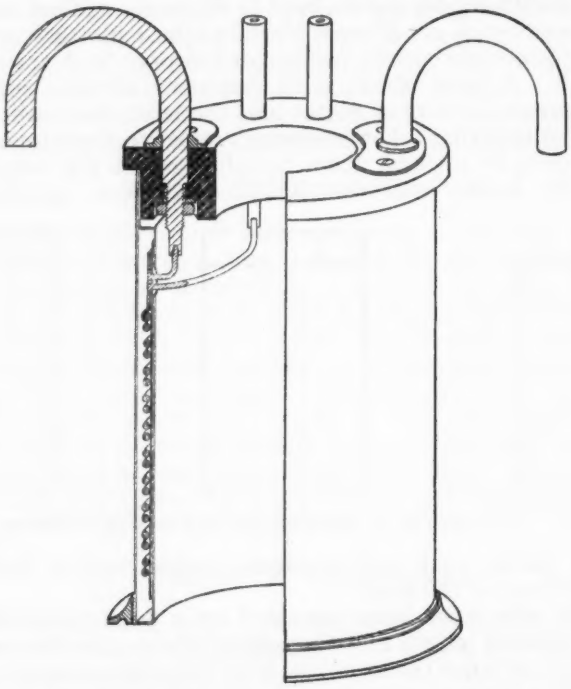


FIGURE 2.—*New type of resistance standard*

in 1,000,000. The greatest part of this change generally takes plac in the first month.

4. The data obtained seem to show that the stability is not affecte by relatively large differences in the composition of the resistanc material.

5. A double-walled sealed container has been designed to be mor permanent and afford better protection from surface action than i given by those of the Rosa type.

VII. ACKNOWLEDGMENTS

Grateful acknowledgement is made to J. A. Scherrer, of the chem istry division, for the chemical analyses of the manganin wire used i the construction of these standards, and to Louis Jordan and W. H Swanger for assistance in annealing the coils.

WASHINGTON, May 5, 1930.

THE STRUCTURE OF THE SPECTRA OF DOUBLY AND TREBLY IONIZED ZIRCONIUM

By C. C. Kiess and R. J. Lang [1]

ABSTRACT

The spectra emitted by Zr atoms which are doubly and trebly ionized have been observed with the grating and prism spectrographs of the National Bureau of Standards and with the vacuum grating spectrograph of the University of Alberta. These spectra have been analyzed and the series relationships involved in them have been established. The terms which have been found to account for the spectra are without exception those required by the quantum theory. Zr IV is a doublet spectrum which results from the migration of a single electron which, in its unexcited state, occupies a 4_3 orbit. From a series of S terms an ionization potential of 33.83 v is derived, corresponding to a value of 274,067 cm^{-1} for the lowest term $4^2D_{\frac{3}{2}}$. Zr III consists of singlet and triplet systems, the terms of which result from the interaction of two electrons occupying 4_3 orbits in their unexcited state. Sequences of ^1D and ^3D terms have been found which result when one of the electrons occupies an n_1 orbit, the other remaining in a 4_3 orbit. These term sequences place the ground term, $^3F_2$, at 194,441 cm^{-1}, which gives 24.00 v as the ionization potential of Zr^{++}. Among the Zr III multiplets are those representing the transition $4f \rightarrow 4d$. These multiplets and also those representing intersystem combinations exhibit anomalous intensities.

CONTENTS

	Page.
I. Introduction	305
II. Experimental procedure	306
III. The spectrum of trebly ionized zirconium (Zr IV)	307
IV. The spectrum of doubly ionized zirconium (Zr III)	309
V. Comparison with Ti IV and Ti III	323
VI. Conclusion and acknowledgments	324

I. INTRODUCTION

The spectra emitted by zirconium electrodes in air, when arc or condensed spark discharges pass between them, have been recognized as emanating from the Zr atom in its neutral and successively ionized stages. Lists of wave lengths of these spectra, covering the range from 9,300 A in the infra-red to 2,160 A in the ultra-violet, were published a few years ago by one of us (C. C. K.).[2] The successful classification of nearly all the stronger lines of these lists into multiplet structures characteristic of Zr I, Zr II, Zr III, and Zr IV revealed the fact that some of the more prominent features of the spectra of doubly and trebly ionized Zr were to be sought for in the Schumann region and beyond. For theoretical reasons, it was obvious that these unknown spectra should contain more lines than were reported by Bowen and Millikan [3] and by McDonald, Sutton, and McLay.[4] Therefore, we planned a new survey of the ultra-violet portions of the spectrum, the region down to 2,000 A to be observed with the Hilger E_1 quartz prism spectrograph at the National Bureau of Standards, the remainder with the vacuum grating spectrograph at the University of Alberta, Edmonton, Canada.

---

[1] Of the department of physics, University of Alberta, Edmonton, Alberta, Canada.
[2] B. S. Sci. Papers, No. 548, **22**, p. 47; 1927.
[3] Phys. Rev., **28**, p. 924; 1926.
[4] Trans. Royal Soc. (Canada) (III), **20**, p. 313; 1926.

II. EXPERIMENTAL PROCEDURE

The electrodes used in this investigation, for both the Bureau of Standards and the University of Alberta observations, were cut from the same rod of zirconium metal kindly supplied to us for spectrographic analysis by Dr. H. C. Rentschler, of the Westinghouse Research Laboratory. It is a pleasure to acknowledge here our indebtedness to him for supplying us with this material, which proved to be of high purity, although containing traces of Fe, Ni, Ti, Al, Sn, Cb, and Si.

For the Bureau of Standards observations, the light sources were either arc or spark discharges maintained between the Zr electrodes. The arcs were operated on 240 volts d. c., at current strengths of 4 or 5 amperes. The spark discharges were supplied by a transformer which stepped-up 110 volts a. c. to 40,000 volts. A condenser of 0.006 μf capacity was connected in parallel across the high-voltage terminals of the transformer. Exposures to the spark were usually juxtaposed to arc exposures, and these in turn to exposures to the Fe or Cu arcs which furnished the comparison spectra.

By setting the prism carriage of the E_1 spectrograph forward 5 cm from the original position, it was possible to photograph the spectrum down to wave length 1,920 A with the aid of Schumann plates. Owing to the lack of reliable standards below 2,000 A no great accuracy is claimed for the Zr wave lengths measured in this region on the Bureau of Standards spectrograms. Above 2,000 A, however, the standards of reference were chosen from both the Fe and Cu arc spectra, for which the wave lengths determined by Burns and Walters [5] and by Mitra,[6] respectively, were used in the reductions. To Doctor Burns we are indebted for a copy of the new Fe standards in advance of publication.

The University of Alberta observations were made with the vacuum spectrograph which has been adequately described elsewhere.[7] Two gratings, each of 2 m radius, were used in this spectrograph to obtain the Zr spectra. For the region 2,100 to 630 A the grating ruled with 30,000 lines per inch and giving a dispersion of 4.5 A per millimeter was employed. The other grating, dispersion 8.5 A per millimeter, was used to photograph the extreme ultra-violet portion between 720 and 280 A. The source, a spark discharge between the Zr terminals supplied by a large X-ray coil, with suitable capacity and an external spark gap in parallel, was operated both in a vacuum and in an atmosphere of hydrogen. The observations in hydrogen, which extend down to 1,470 A, the limit of transparency of the fluorite window which separated the source from the vacuum chamber of the spectrograph, served the very excellent purpose of separating the lines according to the degree of ionization of the radiating atom. Strong lines observed in the hydrogen source but not in the vacuum source were due to Zr^{+}. Lines stronger in hydrogen than in vacuum were due to Zr^{++}, and those stronger in vacuum than in hydrogen were due to the trebly ionized atom. The spectrum as obtained with the vacuum spectrograph is shown in Figure 1.

[5] Pub. Allegheny Observatory, **6**, p. 159; 1929.
[6] Annales de Physique, **19**, p. 315; 1923.
[7] J. Opt. Soc. Am., **12**, p. 523; 1926.

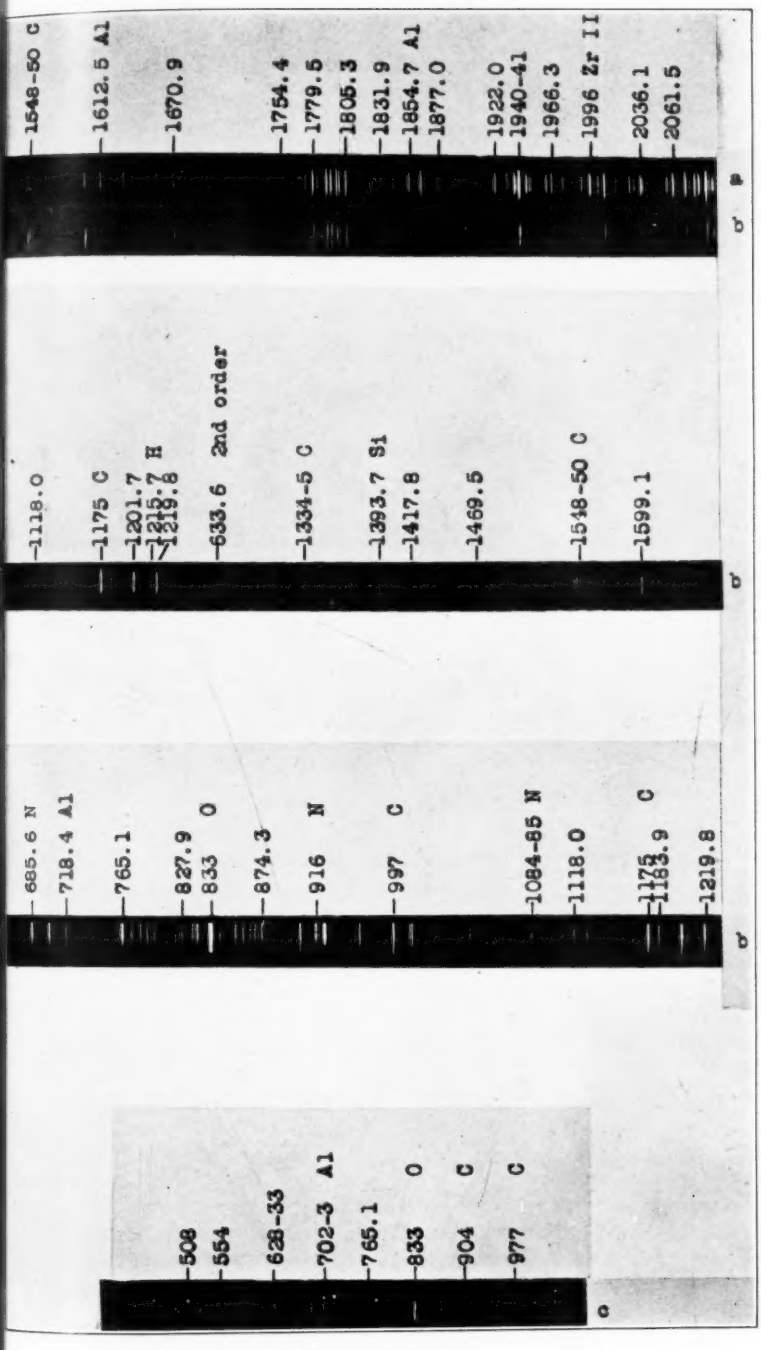


FIGURE 1.—*Vacuum-spark spectrum of zirconium*

III. THE SPECTRUM OF TREBLY IONIZED ZIRCONIUM (Zr IV)

In its normal state the Zr atom has four electrons external to the krypton configuration, two bound in 5_1 "orbits" and two in 4_3 "orbits." The trebly ionized atom has lost all but one of these electrons, namely, one of the 4_3 type, which corresponds to a normal energy state designated by the term ^2D. When the Zr^{+++} ion absorbs energy the lone 4_3 electron is dislodged to any one of the unoccupied orbits in the N, O, and P shells, permitted by the rules governing the transition. The energy states assumed by the atom in this process are designated by the term symbols 5^2S, 5^2P, 4^2F, etc. From their work on the stripped atoms of the second long period, Bowen and Milliken [8] were able to designate for Zr IV not only the normal 4^2D state and the excited 5^2P and 4^2F states which combine with it, but also the states 5^2S and 6^2S which combine with 5^2P. A short-time previously Gibbs and White [9] had already detected the 5S-5P doublet by applying the regular doublet law to the 1-valence-electron systems of the periods beginning with Rb and Cs.

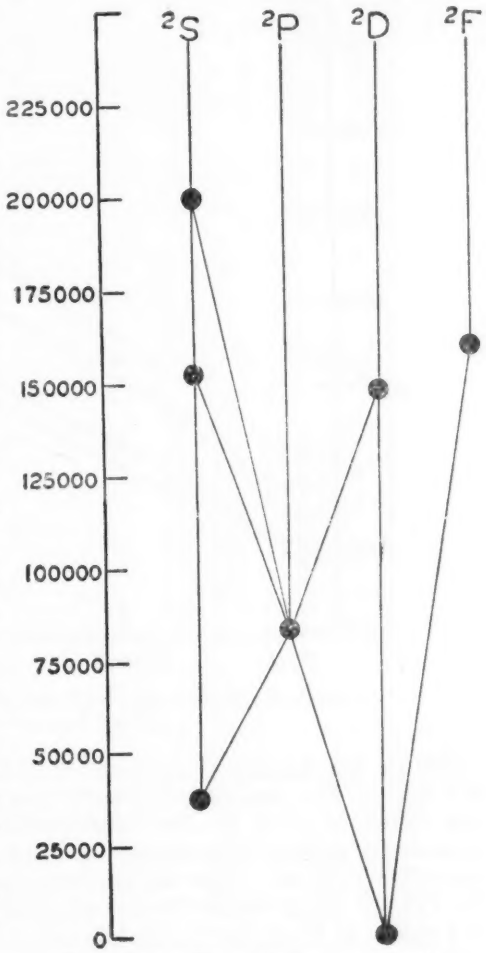


FIGURE 2.—*Term diagram of Zr IV*

To the Zr IV lines thus classified by these earlier investigators we have been able to add a few more. Table 1 contains a list of Zr IV lines which have been definitely established to date, the wave lengths being those derived from the Bureau of Standards and University of Alberta measurements. The terms which account for these lines are given in Table 2, the relative values beginning with 0 for the lowest being entered in the second column. The absolute terms and the Rydberg denominators given in the third and fourth columns result from the series formula

$$mS = 16R/\{m - 2.1237 - 6.1556 \times 10^{-7}\ (mS)\}^2$$

[8] Phys. Rev. **28**, p. 924; 1926.

[9] Proc. Nat. Acad. Sci., **12**, p. 551; 1926.

which has been found to satisfy the terms 5S, 6S, and 7S. We therefore find a value 274,067 cm^{-1} for the ground term $4^2D_{\frac{3}{2}}$ of Zr IV, which gives an ionization potential of 33.83 volts for Zr^{+++}. The relative positions of the Zr IV terms are shown graphically in Figure 2.

The successful application, by various investigators, of the irregular doublet law to corresponding terms arising from the same electron configuration in iso-electronic systems has not only afforded

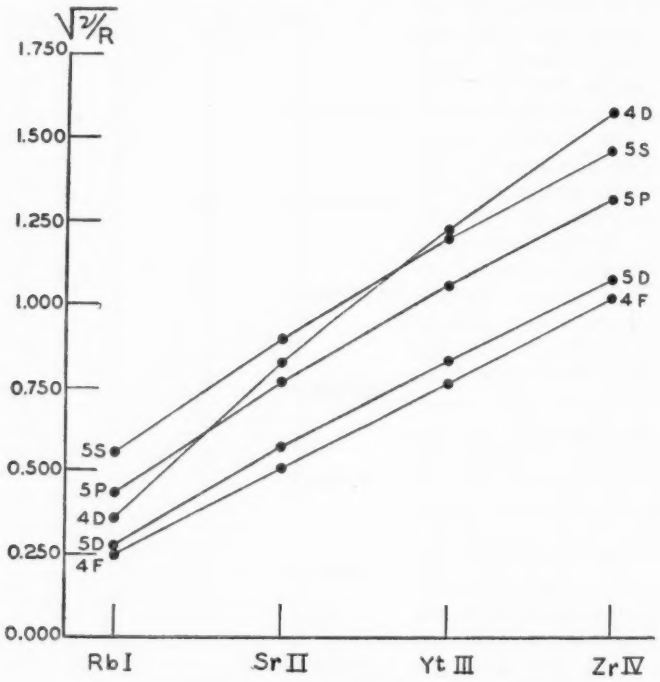


FIGURE 3.—*Values of $\sqrt{\nu/R}$ for the 1 electron systems of the second long period*

check on the identity of the terms, but has established the validity of the law in the domain of optical spectra. According to this law the values of $\sqrt{\nu/R}$ for the corresponding terms should increase by a constant amount with atomic number. Here ν represents the distance between any term and its limit and R is the Rydberg number. In Table 3 are given the values of $\sqrt{\nu/R}$ for the 4D, 4F, 5S, 5P, and 5D terms of Rb I, Sr II, Yt III and Zr IV. Figure 3 shows these values graphically, whence it is seen that although the curves for the terms with total quantum number 5 are sensibly parallel as the law requires, yet that for 4D deviates markedly from parallelism with the curve for 4F. This effect is already apparent in the similar curves based on the data of Russell and Lang [10] for the 4D and 4F terms of K I, Ca II, Sc III, and Ti IV.

[10] Astrophys. J., **66**, p. 13; 1927.

TABLE 1.—*Classified lines of Zr IV*

λ I. A.	Int.	ν	Δν	Term combination
2, 286. 66	15	43, 718. 39	2, 485. 89	$5^2S_{1/2}-5^2P_{1/2}$
2, 163. 62	15	46, 204. 28		$5^2S_{1/2}-5^2P_{3/2}$
1, 608. 02	4	62, 188	351	$5^2P_{3/2}-5^2D_{3/2}$
1, 599. 00	30	62, 539	2, 486	$5^2P_{3/2}-5^2D_{5/2}$
1, 546. 21	20	64, 674		$5^2P_{1/2}-5^2D_{3/2}$
1, 469. 55	15	68, 048	2, 484	$5^2P_{3/2}-6^2S_{1/2}$
1, 417. 78	5	70, 532		$5^2P_{1/2}-6^2S_{1/2}$
1, 219. 85	45	81, 977	2, 483	$4^2D_{3/2}-5^2P_{1/2}$
1, 201. 76	50	83, 211	1, 249	$4^2D_{5/2}-5^2P_{3/2}$
1, 183. 98	25	84, 460		$4^2D_{3/2}-5^2P_{3/2}$
874. 29	10	114, 378	2, 486	$5^2P_{3/2}-7^2S_{1/2}$
855. 69	4	116, 864		$5^2P_{1/2}-7^2S_{1/2}$
633. 56	30	157, 838	1, 230	$4^2D_{5/2}-4^2F_{7/2}$
628. 66	20	159, 068		$4^2D_{3/2}-4^2F_{5/2}$

TABLE 2.—*Terms of Zr IV*

Term type	Relative value	Δν	Absolute value	Rydberg denominator
$4^2D_{3/2}$	0	1, 250	274, 067	2. 5311
$4^2D_{5/2}$	1, 250		272, 817	2. 5369
$5^2S_{1/2}$	38, 258	2, 486	235, 809	2. 7287
$5^2P_{1/2}$	81, 976		192, 091	3. 0232
$5^2P_{3/2}$	84, 462	351	189, 605	3. 0431
$5^2D_{3/2}$	146, 650		127, 417	3. 7121
$5^2D_{5/2}$	147, 001	20	127, 066	3. 7172
$6^2S_{1/2}$	152, 509		121, 558	3. 7976
$4^2F_{5/2}$	159, 068		114, 999	3. 9074
$4^2F_{7/2}$	159, 088		114, 979	3. 9077
$7^2S_{1/2}$	198, 840		75, 227	4. 8275

TABLE 3.—*Values of* $\sqrt{\nu/R}$ *for Rb I, Sr II, Yt III, and Zr IV*

Terms	Rb I	Δ	Sr II	Δ	Yt III	Δ	Zr IV
4D	0. 361	*0. 462*	0. 823	*0. 405*	1. 228	*0. 350*	1. 578
4F	. 251	. *254*	. 505	. *258*	. 763	. *261*	1. 024
5S	. 554	. *346*	. 900	. *298*	1. 198	. *268*	1. 466
5P	. 437	. *332*	. 769	. *289*	1. 058	. *262*	1. 320
5D	. 270	. *300*	. 570	. *265*	. 835	. *242*	1. 077
6S	. 351	. *262*	. 613	. *232*	. 845	. *207*	1. 052

IV. THE SPECTRUM OF DOUBLY IONIZED ZIRCONIUM (Zr III)

A striking feature of the spark spectrum of zirconium in the region extending from 2,900 A to 2,400 A is a group of intense lines which do not appear at all in the arc. Since many of the strong lines of Zr II are readily excited in the arc, it was apparent that these lines are characteristic of a spectrum requiring greater excitation energy than does Zr II. It was soon possible to classify many of them as resulting from combinations of high ^3P, ^3D, and ^3F terms with a

common ^3D term. Accordingly, in the list of Zr wave lengths published a few years ago,[11] they were appropriately designated as belonging to Zr III. The tentative classification of these lines was shortly thereafter communicated to Professors Gibbs and White of Cornell University, who were able not only to verify them, but also to identify the similar combinations of Cb IV by applying the irregular doublet law to the 2-electron systems of Sr I and Yt II. In their paper they suggest an alternative to the term $^3F_4$ communicated to them, which the analysis of the spectrum here presented verifies.

The realization that a richer spectrum exists for Zr III than that represented by the lines just described led to the survey of the far ultra-violet with the University of Alberta vacuum spectrograph, as mentioned above. This survey revealed the strong groups of lines in the regions 2,000 to 1,700 A and 870 to 750 A which involve the low and metastable states of Zr^{++}.

The spectrum of doubly ionized zirconium results from the interaction of the two 4_3 electrons in their normal and excited states. The terms arising from these electrons when unexcited are ^1S, ^1D, ^1G, ^3P, and ^3F, of which the latter is most stable. When one of the electrons is removed to an available unoccupied orbit in the N and O shells, new energy states arise, which, according to theory, are represented by the terms of Table 4.

TABLE 4.—*Theoretical terms of Zr III*

Electron configuration	Terms	
$4d \cdot 4d$	^1S, ^1D, ^1G	^3P ^3F
$4d \cdot 5s$	^1D,	^3D
$4d \cdot 5p$	$^1P°$, $^1D°$, $^1F°$	$^3P°$, $^3D°$, $^3F°$
$4d \cdot 5d$	^1S, ^1P, ^1D, ^1F, ^1G,	^3S, ^3P, ^3D, ^3F ^3G
$4d \cdot 6s$	^1D	^3D
$4d \cdot 4f$	$^1P°$, $^1D°$, $^1F°$, $^1G°$, $^1H°$	$^3P°$, $^3D°$, $^3F°$, $^3G°$, $^3H°$

All the terms of Table 4, except $5d\,^1G$ and $4f\,^3H°$, have been identified for Zr III. The relative values of these terms are given in Table 5. The triplet system terms were established with little or no difficulty, since most of the important multiplets, as shown in Table 7, have their full quota of lines. The fixing of the singlet terms presented a more difficult problem, since only two of them could be located by means of intersystem combinations. The detection, however, of the triplet multiplets (Table 8) coming from the $4f$ electron furnished the key to the problem. For, the singlet P, D, and F terms, coming from $4f$ and those from $5p$ must combine with the $4d$ singlets to give pairs of lines separated by the $\Delta\nu$'s of the $4d$ singlets. With these pairs of lines located, the only remaining pair of strong lines in the far ultra-violet was regarded as coming from the singlet G° and H° terms. A similar procedure was followed to locate the $5d$ and $6s$ singlet terms. The classification of Zr III lines on the basis of these terms is given in Table 6, in which the term symbols are expressed in the notation recently proposed

[11] B. S., Sci. Papers, No. 548, **22**, p. 57; 1927. [12] Phys. Rev., **31**, p. 520; 1928.

as standard by Russell, Shenstone, and Turner.[13] The letter *b* following the intensity estimate of a line indicates that it is nebulous usually a property of lines originating in the high-energy levels of the atom. The letter *d* indicates that the line is double.

TABLE 5.—*Terms of Zr III*

Term No.	Term type	ν	$\Delta\nu$	Electron configuration	Term No.	Term type	ν	$\Delta\nu$	Electron configuration
1	$^3F_2$	0	682.5		32	$^3D_1$	?		
2	$^3F_3$	682.5	804.3		33	$^3D_2$	97,462.0	−31.3	
3	$^3F_4$	1,486.8			34	$^3D_3$	97,430.7		
4	$^1G_4$	2,534			35	$^3P_0$	97,918.2	−5.7	
5	$^1D_2$	3,392		4d·4d.	36	$^3P_1$	97,912.5	784.5	
6	$^1S_0$	3,835			37	$^3P_2$	98,697.0		4d·5d.
7	$^3P_0$	8,061.4	265.4		38	$^3F_2$	103,839.6	632.1	
8	$^3P_1$	8,326.8	513.2		39	$^3F_3$	104,471.7	1,116.6	
9	$^3P_2$	8,840.0			40	$^3F_4$	105,588.3		
10	$^1D_2$	16,122.5			41	$^3G_3$	104,635.8	556.2	
11	$^3D_1$	18,398.6	403.9	4d·5s.	42	$^3G_4$	105,192.0	1,112.4	
12	$^3D_2$	18,802.5	730.7		43	$^3G_5$	106,304.4		
13	$^3D_3$	19,533.2			44	$^1D_2$	107,631.5		
14	$^1D°_2$	53,170.0			45	$^3D_1$	107,309.3	507.7	
15	$^1P°_1$	53,646.7			46	$^3D_2$	107,817.0		4d·6s.
16	$^1F°_3$	54,071.5			47	$^3D_3$	108,313.0	496.0	
17	$^3F°_2$	55,554.9			48	$^1P°_1$	127,320		
18	$^3F°_3$	56,074.7	519.8		49	$^1D°_2$	126,531		
19	$^3F°_4$	57,681.4	1,606.7		50	$^1F°_3$	131,736		
				4d·5p.	51	$^1G°_4$	131,406		
20	$^3D°_1$	55,613.3			52	$^1H°_5$	130,002		
21	$^3D°_2$	56,435.5	822.2		53	$^3F°_2$	121,466		
22	$^3D°_3$	57,346.4	910.9		54	$^3F°_3$	119,526	−1,940	
23	$^3P°_0$	59,945.6			55	$^3F°_4$	117,814	−1,712	
			−248.1		56	$^3G°_3$	122,015		
24	$^3P°_1$	59,697.5	658.9					588	4d·4f.
25	$^3P°_2$	60,356.4			57	$^3G°_4$	122,603	400	
26	$^1S_0$	88,999			58	$^3G°_5$	123,003		
27	$^1P_1$	97,879			59	$^3P°_0$	123,392	202	
					60	$^3P°_1$	123,594	362	
28	$^1D_2$	98,058		4d·5d.					
29	$^1F_3$	101,413			61	$^3P°_2$	123,956		
30	$^1G_4$	?			62	$^3D°_1$	131,008	510	
31	$^1S_1$	94,767.3			63	$^3D°_2$	131,518	680	
					64	$^3D°_3$	132,198		

TABLE 6.—*Classified lines of Zr III*

λ I. A.	Intensity and notes	ν	Term combinations
3,021.21	2*b*	33,089.71	$5d^3P_0$–$4f^3D°_1$
2,984.09	3*b*	33,501.31	$5d^3P_2$–$4f^3D°_3$
2,974.85	2*b*	33,605.36	$5d^3P_1$–$4f^3D°_2$
2,870.95	1*b*	34,821.48	$5p^3P°_0$–$5d^3S_1$
2,869.06	7	34,844.42	$5s^3D_2$–$5p^1P°_1$
2,850.62	3*b*	35,069.81	$5p^3P°_1$–$5d^3S_1$
2,836.19	10	35,248.22	$5s^3D_1$–$5p^1P°_1$
2,827.90	3	35,351.55	$5p^1P°_1$–$5d^1S_0$
2,775.26	5	36,022.05	$5s^3D_3$–$5p^3F°_2$
2,735.79	20	36,541.72	$5s^3D_3$–$5p^3F°_3$
2,720.08	7	36,752.75	$5s^3D_2$–$5p^3F°_2$
2,715.76	18	36,811.22	$5s^3D_2$–$5p^3D°_1$
2,709.06	18	36,902.25	$5s^3D_2$–$5p^3D°_2$
2,698.31	15	37,049.26	$5s^1D_2$–$5p^1D°_2$
2,696.50	2	37,074.13	$5p^3P°_2$–$5d^3D_3$

[13] Phys. Rev., **33**, p. 900; 1929.

TABLE 6.—*Classified lines of Zr III*—Continued

λ I. A.	Intensity and notes	ν	Term combinations
2, 690. 51	20	37, 156. 66	$5s^3D_1$–$5p^3F°_2$
2, 686. 30	20	37, 214. 89	$5s^3D_1$–$5p^3D°_1$
2, 682. 18	20	37, 272. 05	$5s^3D_2$–$5p^3F°_3$
2, 664. 27	20	37, 522. 59	$5s^1D_2$–$5p^1P°_1$
2, 661. 90	3	37, 555. 99	$5p^3P°_2$–$5d^3P_1$
2, 656. 48	20	37, 632. 62	$5s^3D_2$–$5p^3D°_2$
2, 647. 24	1	37, 763. 96	$5p^3P°_1$–$5d^3D_2$
2, 643. 83	20	37, 812. 66	$5s^3D_3$–$5p^3D°_3$
2, 634. 33	8	37, 949. 02	$5s^1D_2$–$5p^1F°_3$
2, 633. 09	1	37, 966. 89	$5p^3P°_0$–$5d^3P_1$
2, 628. 28	20	38, 036. 36	$5s^3D_1$–$5p^3D°_2$
2, 620. 57	40	38, 148. 27	$5s^3D_3$–$5p^3F°_4$
2, 615. 99	4	38, 215. 05	$5p^3P°_1$–$5d^3P_1$
2, 615. 60	4	38, 220. 75	$5p^3P°_1$–$5d^3P_0$
2, 608. 73	3*b*	38, 321. 39	$5d^1S_0$–$4f^1P°_1$
2, 607. 42	3*b*	38, 340. 64	$5p^3P°_2$–$5d^3P_2$
2, 593. 68	20	38, 543. 74	$5s^3D_2$–$5p^3D°_3$
2, 563. 40	3	38, 999. 01	$5p^3P°_1$–$5d^3P_2$
2, 502. 37	1*b*	39, 950. 07	$5s^1D_2$–$5p^3F°_3$
2, 494. 00	5	40, 084. 14	$5p^3D°_3$–$5d^3D_3$
2, 492. 08	2	40, 115. 02	$5p^3D°_3$–$5d^3D_2$
2, 448. 86	40	40, 822. 96	$5s^3D_3$–$5p^3P°_2$
2, 444. 57	25	40, 894. 69	$5s^3D_2$–$5p^3P°_1$
2, 438. 65	2*d*?	40, 993. 85	$5p^3D°_2$–$5d^3D_3$
2, 436. 68	1	41, 026. 99	$5p^3D°_2$–$5d^3D_2$
2, 420. 62	20	41, 299. 18	$5s^3D_1$–$5p^3P°_1$
2, 406. 18	10	41, 547. 00	$5s^3D_1$–$5p^3P°_0$
2, 405. 78	12	41, 553. 91	$5s^3D_2$–$5p^3P°_2$
2, 382. 60	4	41, 958. 14	$5s^3D_1$–$5p^3P°_2$
2, 260. 11	2*b*	44, 231. 91	$5s^1D_2$–$5p^3P°_2$ $5p^1P°_1$–$5d^1P_1$
2, 250. 99	3*b*	44, 411. 09	$5p^1P°_1$–$5d^1D_2$
2, 235. 96	1	44, 709. 59	$5p^1D°_2$–$5d^1P_1$
2, 227. 05	3*b*	44, 888. 45	$5p^1D°_2$–$5d^1D_2$
2, 203. 58	3*b*	45, 366. 49	$5p^3F°_3$–$5d^1F_3$
2, 178. 46	2*b*	45, 889. 56	$5p^3F°_4$–$5d^1F_3$
2, 139. 86	3	46, 717. 25	$4d^3P_2$–$5p^3F°_2$
2, 129. 12	1	46, 952. 87	$5p^3F°_4$–$5d^3G_3$
2, 116. 63	4	47, 229. 90	$4d^3P_1$–$5p^3F°_2$
2, 116. 32	4	47, 236. 82	$4d^3P_2$–$5p^3F°_3$
2, 114. 07	6	47, 287. 08	$4d^3P_1$–$5p^3D°_1$
2, 104. 26	1*b*	47, 507. 51	$5p^3F°_4$–$5d^3G_4$
2, 102. 27	10	47, 552. 47	$4d^3P_0$–$5p^3D°_1$
2, 100. 28	2	47, 597. 52	$4d^3P_2$–$5p^3D°_2$
2, 092. 97	2	47, 763. 75	$5p^3F°_3$–$5d^3F_2$
2, 086. 72	25	47, 906. 78	$5p^3F°_4$–$5d^3F_4$
2, 077. 83	12	48, 111. 73	$4d^3P_1$–$5p^3D°_2$
2, 070. 86	5	48, 273. 64	$5p^1D°_2$–$5d^1F_3$
2, 070. 34	12	48, 285. 76	$5p^3F°_2$–$5d^3F_2$
2, 065. 60	8	48, 396. 55	$5p^3F°_3$–$5d^3F_3$
2, 060. 69	15	48, 511. 84	$4d^3P_2$–$5p^3D°_3$

TABLE 6.—*Classified lines of Zr III*—Continued

λ I. A.	Intensity and notes	ν	Term combinations
2, 058. 57	3*b*	48, 561. 80	$5p^3F^\circ_3$–$5d^3G_3$
2, 055. 98	8*b*	48, 622. 97	$5p^3F^\circ_4$–$5d^3G_5$
2, 043. 61	1	48, 917. 24	$5p^3F^\circ_2$–$5d^3F_3$
2, 036. 76	4*b*	49, 081. 74	$5p^3F^\circ_2$–$5d^3G_3$
2, 035. 26	6*b*	49, 117. 90	$5p^3F^\circ_3$–$5d^3G_4$
2, 018. 99	0	49, 513. 66	$5p^3F^\circ_3$–$5d^3F_4$
2, 008. 17	1*b*	49, 780. 40	$4d^1D_2$–$5p^1D^\circ_2$
2, 006. 74	12	49, 815. 87	$4d^1S_0$–$5p^1P^\circ_1$
1, 989. 87	15	50, 254	$4d^1D_2$–$5p^1P^\circ_1$
1, 975. 00	8	50, 632	$5p^3F^\circ_4$–$6s^3D_3$
1, 966. 29	20	50, 857	$4d^3P_2$–$5p^3P^\circ_1$
1, 962. 07	10	50, 966	$5p^3D^\circ_3$–$6s^3D_3$
1, 946. 66	10	51, 370	$4d^3P_1$–$5p^3P^\circ_1$
1, 946. 09	4	51, 380	$5p^3D^\circ_2$–$6s^3D_2$
1, 941. 15	40	51, 515	$4d^3P_2$–$5p^3P^\circ_2$
1, 940. 32	40	51, 537	$4d^1G_4$–$5p^1F^\circ_3$
1, 937. 29	15	51, 618	$4d^3P_1$–$5p^3P^\circ_0$
1, 936. 63	15	51, 636	$4d^3P_0$–$5p^3P^\circ_1$
1, 934. 35	2	51, 696	$5p^3D^\circ_1$–$6s^3D_1$
1, 932. 58	4	51, 744	$5p^3F^\circ_3$–$6s^3D_2$
1, 922. 02	20	52, 028	$4d^3P_1$–$5p^3P^\circ_2$
1, 914. 07	0	52, 244	$5p^3F^\circ_3$–$6s^3D_3$
1, 885. 28	2	53, 042	$4d^1D_2$–$5p^3D^\circ_2$
1, 867. 04	3	53, 560	$5p^1F^\circ_3$–$6s^1D_2$
1, 864. 06	20	53, 646	$4d^3F_2$–$5p^1P^\circ_1$
1, 853. 43	8	53, 954	$4d^1D_2$–$5p^3D^\circ_3$
1, 836. 13	0	54, 462	$5p^1D^\circ_2$–$6s^1D_2$
1, 831. 88	4	54, 588	$4d^3F_4$–$5p^3F^\circ_3$
1, 805. 33	30	55, 391	$4d^3F_3$—$5p^3F^\circ_3$
1, 800. 04	20	55, 554	$4d^3F_2$–$5p^3F^\circ_2$
1, 798. 16	30	55, 612	$4d^3F_2$–$5p^3D^\circ_1$
1, 793. 64	30	55, 752	$4d^3F_3$–$5p^3D^\circ_2$
1, 790. 24	30	55, 858	$4d^3F_4$–$5p^3D^\circ_3$
1, 783. 34	5	56, 074	$4d^3F_2$–$5p^3F^\circ_3$
1, 779. 55	30	56, 193	$4d^3F_4$–$5p^3F^\circ_4$
1, 771. 96	5	56, 434	$4d^3F_2$–$5p^3D^\circ_2$
1, 764. 80	1	56, 663	$4d^3F_3$–$5p^3D^\circ_3$
1, 754. 44	6	56, 998	$4d^3F_3$–$5p^3F^\circ_4$
1, 675. 81	0	59, 672	$4d^3F_3$–$5p^3P^\circ_2$
1, 675. 20	0	59, 694	$4d^3F_2$–$5p^3P^\circ_1$
871. 46	5	114, 749	$4d^3P_2$–$4f^3P^\circ_1$
869. 07	5	115, 065	$4d^3P_1$–$4f^3P^\circ_0$
868. 67	5	115, 118	$4d^3P_2$–$4f^3P^\circ_2$
867. 55	4	115, 267	$4d^3P_1$–$4f^3P^\circ_1$
865. 52	4	115, 537	$4d^3P_0$–$4f^3P^\circ_1$
864. 85	6	115, 626	$4d^3P_1$–$4f^3P^\circ_2$
859. 64	12	116, 327	$4d^3F_4$–$4f^3F^\circ_4$
853. 74	10	117, 131	$4d^3F_3$–$4f^3F^\circ_4$
841. 44	12	118, 843	$4d^3F_3$–$4f^3F^\circ_3$
836. 62	5	119, 528	$4d^3F_2$–$4f^3F^\circ_3$

TABLE 6.—*Classified lines of Zr III*—Continued

λ I. A.	Intensity and notes	ν	Term combinations
827. 93	12	120, 783	$4d^3F_3$–$4f^3F^\circ_2$
825. 67	3	121, 113	$4d^3F_4$–$4f^3G^\circ_4$
824. 19	3	121, 331	$4d^3F_3$–$4f^3G^\circ_3$
823. 60	20*d*	121, 418	$4d^3F_2$–$4f^3F^\circ_2$
822. 11	14	121, 516	$4d^3F_4$–$4f^3G^\circ_5$
820. 20	12	121, 921	$4d^3F_3$–$4f^3G^\circ_4$
819. 57	12	122, 015	$4d^3F_2$–$4f^3G^\circ_3$
812. 09	15	123, 139	$4d^1D_2$–$4f^1D^\circ_2$
809. 80	12	123, 487	$4d^1S_0$–$4f^1P^\circ_1$
806. 93	12	123, 926	$4d^1D_2$–$4f^1P^\circ_1$
784. 51	18	127, 468	$4d^1G_4$–$4f^1H^\circ_5$
779. 15	12	128, 344	$4d^1D_2$–$4f_1F^\circ_3$
775. 96	8	128, 872	$4d^1G_4$–$4f^1G^\circ_4$
773. 98	1	129, 202	$4d^1G_4$–$4f^1F^\circ_3$
765. 11	30	130, 700	$4d^3F_4$–$4f^3D^\circ_3$
764. 33	15	130, 833	$4d^3F_3$–$4f^3D^\circ_2$
763. 30	10	131, 010	$4d^3F_2$–$4f^3D^\circ_1$
760. 43	3	131, 504	$4d^3F_3$–$4f^3D^\circ_3$
756. 48	0	132, 191	$4d^3F_2$–$4f^3D^\circ_3$

TABLE 7.—*Triplet system multiplets from the transitions 5p—5d and 5p—5s*

TABLE 7.—*Triplet system multiplets from the transitions 5p→4d and 5p→5s*

	$4d^3F_2$	682.5 $4d^3F_3$	804.3 $4d^3F_4$	$4d^3P_0$	265.4 $4d^3P_1$	513.2 $4d^3P_2$	$5s^3D_1$	403.9 $5s^3D_2$	730.7 $5s^3D_3$
		6	30						40
$5p^3F°_4$		1, 754. 44	1, 779. 55						2, 620. 57
1,606.7		56, 998	56, 193						38, 148. 27
	5	30	4			4		20	20
$5p^3F°_3$	1, 783. 34	1, 805. 33	1, 831. 88			2, 116. 32		2, 682. 18	2, 735. 79
519. 8	56, 074	55, 391	54, 588			47, 236. 82		37, 272. 05	36, 541. 72
	20				4	3	20	7	5
$5p^3F°_2$	1, 800. 04	{ 1, 822. 4			2, 116. 63	2, 139. 86	2, 690. 51	2, 720. 08	2, 775. 26
	55, 554	{54, 872 }			47, 229. 90	46, 717. 25	37, 156. 66	36, 752. 75	36, 022. 05
		1	30			15		20	20
$5p^3D°_3$	{ 1, 743. 8 }	1, 764. 80	1, 790. 24			2, 060. 69		2, 593. 68	2, 643. 83
910. 9	{57, 346 }	56, 663	55, 858			48, 511. 84		38, 543. 74	37, 812. 66
	5	30			12	2	20	20	18
$5p^3D°_2$	1, 771. 96	1, 793. 64			2, 077. 83	2, 100. 28	2, 628. 28	2, 656. 48	2, 709. 06
822. 2	56, 434	55, 752			48, 111. 73	47, 597. 52	38, 036. 36	37, 632. 62	36, 902. 25
	30			10	6		20	18	
$5p^3D°_1$	1, 798. 16			2, 102. 27	2, 114. 07	{ 2, 137. 3 }	2, 686. 30	2, 715. 76	
	55, 612			47, 552. 47	47, 287. 08	{46, 773. 9 }	37, 214. 89	36, 811. 22	
		0			20	40	4	12	40
$5p^3P°_2$	{ 1, 656. 9 }	1, 675. 81			1, 922. 02	1, 941. 15	2, 382. 60	2, 405. 78	2, 448. 86
658. 9	{60, 354 }	59, 672			52, 028	51, 515	41, 958. 14	41, 553. 91	40, 822. 96
	0			15	10	20	20	25	
$5p^3P°_1$	1, 675. 20			1, 936. 63	1, 946. 66	1, 966. 29	2, 420. 62	2, 444. 57	
−248.1	59, 694			51, 636	51, 370	50, 857	41, 299. 18	40, 894. 69	
					15		10		
$5p^3P°_0$					1, 937. 29		2, 406. 18		
					51, 618		41, 547. 00		
	20						10	12	
$5p^1P°_1$	1, 864. 06			{ 2, 193. 0 }	{ 2, 205. 9 }	{ 2, 231. 1 }	2, 836. 19	2, 869. 06	
	53, 646			{45, 585 }	{45, 319 }	{44, 806 }	35, 248. 22	34, 844. 42	

TABLE 8.—*Multiplets from the transition 4f→4d*

4f \ 4d	$^3F_2$	682.5 $^3F_3$	804.3 $^3F_4$	$^3P_0$	265.4 $^3P_1$	513.2 $^3P_2$
$^3G°_5$			14 822. 11 121, 516			
$^3G°_4$		12 820. 20 121, 921	3 825. 67 121, 113			
$^3G°_3$	12 819. 57 122, 015	3 824. 19 121, 331	{829. 69} {120, 527}			
$^3F°_4$		10 853. 74 117, 131	12 859. 64 116, 327			
$^3F°_3$	5 836. 62 119, 528	12 841. 44 118, 843	{847. 18} {118, 039}			
$^3F°_2$	12? [1] 823. 28 121, 466	12 827. 93 120, 783				
$^3D°_3$	0 756. 48 132, 191	3 760. 43 131, 504	30 765. 11 130, 700			
$^3D°_2$	3 760. 43 131, 504	15 764. 33 130, 833				
$^3D°_1$	10 763. 30 131, 010					

	760. 43 131, 504	764. 33 130, 833			
$^3D^o_1$	10 763. 30 131, 010				
$^3P^o_2$				6 864. 85 115, 626	5 868. 67 115, 118
$^3P^o_1$			4 865. 52 115, 537	4 867. 55 115, 267	5 871. 46 114, 749
$^3P^o_0$				5 869. 07 115, 065	

[1] Calculated wave length. The observed line at 823.60 A is blended with another strong line.

TABLE 9.—*Multiplets from the transition 5d→5p*

	$5p^3F^\circ_3$	519.8 $5p^3F^\circ_3$	1,606.7 $5p^3F^\circ_4$	$5p^3D^\circ_1$	822.2 $5p^3D^\circ_2$	910.9 $5p^3D^\circ_3$	$5p^3P^\circ_0$	−248.1 $5p^3P^\circ_1$	658.9 $5p^3P^\circ_2$
			8*b*						
$5d^3G_5$			2, 055. 98						
			48, 622. 97						
1,112.4									
		6*b*	1*b*						
$5d^3G_4$		2, 035. 26	2, 104. 26						
		49, 117. 90	47, 507. 51						
556.2									
	4*b*	3*b*	1						
$5d^3G_3$	2, 036. 76	2, 058. 57	2, 129. 12						
	49, 081. 74	48, 561. 80	46, 952. 87						
		0	25						
$5d^3F_4$		2, 018. 99	2, 086. 72						
		49, 513. 66	47, 906. 78						
1,116.6									
	1	8	{ 2, 136. 5 }						
$5d^3F_3$	2, 043. 61	2, 065. 60	{ 46, 789. 9 }						
	48, 917. 24	48, 396. 55							
632.1									
	12	2							
$5d^3F_2$	2, 070. 34	2, 092. 97							
	48, 285. 76	47, 763. 75							
					2*d*?	5			2
$5d^3D_3$					2, 438. 65	2, 494. 00			2, 696. 50
					40, 993. 85	40, 084. 14			37, 074. 13
−31.3									
					1	2		1	
$5d^3D_2$				{ 2, 388. 8 }	2, 436. 68	2, 492. 08		2, 647. 24	{ 2, 694. 2 }
				{ 41, 849. 2 }	41, 026. 99	40, 115. 02		37, 763. 96	{ 37, 105. 6 }
?									
$5d^3D_1$				(?)	(?)		(?)	(?)	(?)

$5d^3P_2$				3 2, 563. 40 38, 999. 01		3b 2, 607. 42 38, 340. 64	
784.5							
$5d^3P_1$		1 2, 633. 09 37, 966. 89		4 2, 615. 99 38, 215. 05		3 2, 661. 90 37, 555. 99	
— 5.7							
$5d^3P_0$				4 2, 615. 60 38, 220. 75			

Inspection of Table 5 will reveal several pairs of terms which may be used for calculating series limits. These are shown to better advantage in Figure 4 in which terms of the same L value and of like parity are plotted on the same vertical line. Experience has shown that terms arising from the *nd* electrons are not satisfactorily represented by a simple Rydberg formula, which is theoretically accounted

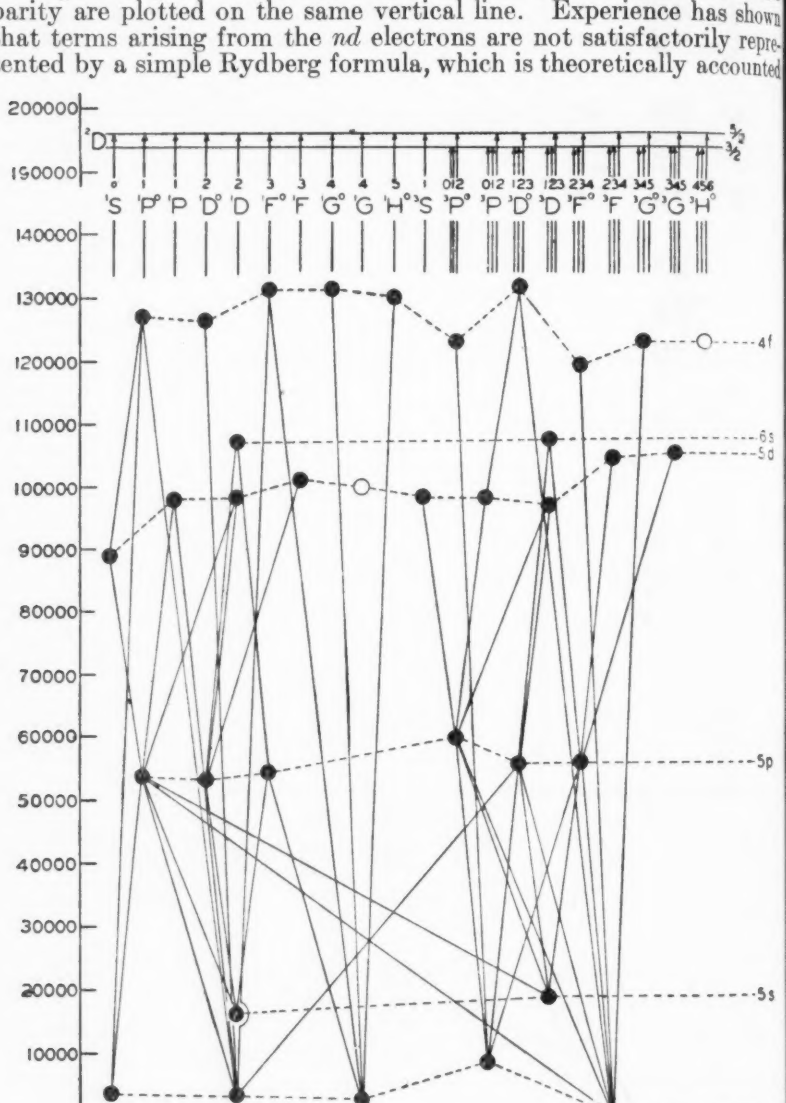


FIGURE 4.—*Term diagram of Zr III*

for by the strength with which the d electron of least n is bound in its orbit. That terms arising from configurations without s electrons tend to become more stable with increasing core charge was pointed out several years ago by Laporte [14] for the heavier atoms of the second long period. More recently Laporte and Lang [15] have demonstrated a similar property for the iso-electronic systems of Ni, Cu^+, and Zn^{++}.

[14] J. Opt. Soc. Am., **13**, p. 1; 1926.

[15] Phys. Rev., **30**, p. 378; 1928.

To establish the absolute term values of Zr III and to calculate the ionization potential of Zr^{++} we therefore make use of the sequences of ^1D and ^3D terms coming from the *ns* electrons. The manner in which the component series approach their limits in Zr IV is illustrated in the upper portion of Figure 4, which is taken from Hund.[16] The series of $^1D_2$ terms and those of $^3D_2$ terms both converge to $^2D_5/_2$ of Zr IV, whereas the series of $^3D_2$ and $^3D_1$ both converge to $^2D_3/_2$. In Table 10 we give the values for the series limits of Zr III as found by simple interpolation from Table III of Fowler's Report on Series in Line Spectra. The separation of the ground states of Zr III and Zr IV proves to be 194,441 cm^{-1}, which gives 24.00 v as the potential required to convert the doubly ionized Zr atom into the trebly ionized atom.

TABLE 10.—*Series limits of Zr III*

Term sequence	Limiting term of Zr IV		$^3F_2$—$^2D_3/_2$
	$^2D_3/_2$	$^2D_5/_2$	
ns $^1D_2$		195, 978	194, 728
ns $^3D_3$		195, 195	193, 945
ns $^3D_2$	194, 824		194, 824
ns $^3D_1$	194, 268		194, 268
Means	194, 546	195, 586	194, 441

$^2D_5/_2$—$^2D_3/_2$ { observed: 1,250 cm^{-1} ; calculated: 1,040 cm^{-1}

I. P. $= 1{,}2345 \times 194{,}441 \times 10^{-4} = 24.00$ v.

In comparing the corresponding terms of Rb I, Sr II, Yt III, and Zr IV by means of the irregular doublet law it was noted above that the increase in value of the term 4^2D is anomalous. Therefore it becomes of interest to see to what extent the law holds for the spectra Sr I, Yt II, and Zr III, of the second long period, in view of the fact that Russell and Lang, in the work cited above, have shown its validity for the spectra Ca I, Sc II, and Ti III, of the first long period. That we may expect it to hold, at least approximately, for some of the terms is evident from the work of Gibbs and White, already referred to, who were able to detect with its aid the triplet system multiplets representing the electron transition $4d5p \rightarrow 4d5s$ both for Zr III and Cb IV.

Table 11 presents a comparison of the values of $\sqrt{\nu/R}$ calculated for corresponding terms of neutral Sr, singly ionized Yt, and doubly ionized Zr. The data for Sr I were taken from the analysis given by Russell and Saunders.[17] For Yt II the data were taken from the analysis given by Meggers and Russell.[18] The differences between the values of $\sqrt{\nu/R}$ for the terms belonging to the same configuration do not run as smoothly as previous comparisons of the kind for other atomic systems would indicate. The criticism may be raised at once

[16] Linienspektren und periodisches System der Elemente, p. 198; 1927. Julius Springer, Berlin.
[17] Astrophys. J., **61**, p. 38; 1925.
[18] B. S. Jour. Research, **2**, p. 733; 1929.

that some of the terms may not be correctly identified. The possi bility of this, especially for singlet terms, is recognized. Thus, th difference 0.346 for the term $^1F^\circ_3$ of the $5p$ configuration appears to b too high. On this term depends the position of $4d^1G_4$, whose differ ence 0.445 also seems too high when compared with the differenc 0.415 given by the well-established $^3P_2$ and $^3F_4$ terms of the $4d^2$ con figuration. But if we compute the hypothetical positions of $4d^1G$ and also $4d^1D$, by assuming the difference 0.415 to hold for them as fo the triplet terms, we get terms which require strong lines in region of the spectrum where there are none and leave unclassified the stron lines which have been accounted for on the basis of the terms o Table 5. The term $4d^1D$, whose difference 0.438 appears too high i comparison with the 0.415 of the ^3P and ^3F terms, is, however, well established through intersystem combinations.

TABLE 11.—*Comparison of Sr I, Yt II, and Zr III*

Electron configuration	Term	$\sqrt{\nu/R}$				
		Sr I	Δ	Yt II	Δ	Zr III
$4d.4d$	$^3F_4$			0. 917	*0. 414*	1. 331
	$^3P_2$	0. 382	*0. 508*	. 890	*. 415*	1. 305
	$^1G_4$			. 882	*. 445*	1. 327
	$^1D_2$			. 886	*. 438*	1. 324
	$^1S_0$					1. 323
$4d.5s$	$^3D_3$	. 622	*. 331*	. 953	*. 311*	1. 264
	$^1D_2$	. 609	*. 335*	. 944	*. 331*	1. 275
$4d.5p$	$^3F^\circ_4$	. 495	*. 323*	. 818	*. 304*	1. 122
	$^3D^\circ_3$	. 470	*. 343*	. 813	*. 310*	1. 123
	$^3P^\circ_2$	. 462	*. 334*	. 796	*. 315*	1. 111
	$^1F^\circ_3$			. 790	*. 346*	1. 136
	$^1D^\circ_2$			. 830	*. 310*	1. 140
	$^1P^\circ_1$			. 823	*. 315*	1. 138
$4d.5d$	$^3G_5$			. 618	*. 285*	. 903
	$^3F_4$			. 602	*. 304*	. 906
	$^3D_3$			. 622	*. 325*	. 947
	$^3P_2$			. 582	*. 358*	. 940
	$^3S_1$			. 608	*. 351*	. 959
	$^1G_4$			. 592		
	$^1F_3$			. 628	*. 299*	. 927
	$^1D_2$			. 613	*. 331*	. 944
	$^1P_1$			. 619	*. 325*	. 944
	$^1S_0$			. 620	*. 366*	. 986
$4d.6s$	$^3D_3$			. 648	*. 245*	. 893
	$^1D_2$			. 648	*. 248*	. 896

Among the triplet terms of the $5d$ group the differences betwee the $\sqrt{\nu/R}$ of Yt II and Zr III range from 0.285 to 0.358. The reality of the terms is, however, well attested by the multiplets resultin from their combination with the triplet terms of the $5p$ electron which give well-established satellite separations. It is not surprising therefore, that the singlet terms of the same configuration exhibi the same range in the differences between the $\sqrt{\nu/R}$ values. It thus seems highly probable that the spectral terms of the heavier atomic systems conform only approximately to the irregular doublet law.

V. COMPARISON WITH Ti IV AND Ti III

The main features of the analysis of Zr IV and Zr III presented in this paper closely resemble those found for Ti IV and Ti III by Russell and Lang.[19] But there are some differences between the spectra of the two elements deserving remark. The Zr multiplets are all of longer wave length than their Ti counterparts, owing to the contraction of the Zr term structure as compared with that of Ti. This fact is responsible for bringing into the domain of observation the 4*f* multiplets of Zr III which are missing from Ti III and for placing beyond observation the 5D-4F combination of Zr IV which has been observed for Ti IV. In Zr III the metastable singlet terms of the $4d^2$ configuration all lie close together with ^1G lowest, whereas in Ti III both ^1S and ^1G are approximately 6,000 cm^{-1} above ^1D. Of the Zr III terms, ^1D and ^3D, coming from the 5*s* electron, the singlet term is the lower; in Ti III the triplet term lies lower. This characteristic of the Zr III terms is, however, confirmed by the analysis of Zr II (to be presented in a subsequent paper in this Journal). Each of them serves as the limit of series of doublet P, D, and F terms of Zr II obtained by adding *p* electrons to the 4*d* 5*s* configuration. Two triads coming from 4*d* 5*s* 5*p* have been found in Zr II, separated by approximately 10,000 cm^{-1}. In the lower triad the component terms are separated by small $\Delta\nu$'s, indicating their origin in a singlet term, whereas in the higher triad the $\Delta\nu$'s are large, which indicates their origin in the triplet term.

A further point of difference between Zr III and Ti III is in the character of the intersystem combinations. In Ti III the observed lines of this class are all faint; in Zr III they are strong. According to Kronig's [20] extension of Sommerfeld's qualitative intensity rule those term combinations are most intense for which the change, ΔL, in the quantum numbers of the terms is the same as the change, Δk, in the azimuthal quantum number of the series electron. Two of the intersystem multiplets of Zr III represent combinations which should be weak or missing according to this rule, and combinations which we might expect to occur, and do occur faintly in Ti III, are missing from Zr III.

This departure from the intensity rule is apparent also among the 4*f*–4*d* multiplets, Table 8. Here the combination $^3D^\circ \rightarrow {}^3F$ is clearly stronger than the $^3G^\circ \rightarrow {}^3F$ combination, and $^3P^\circ \rightarrow {}^3P$ is present with moderate intensity, whereas the expected $^3D^\circ \rightarrow {}^3P$ multiplet is missing. Unfortunately the corresponding multiplets of Ti III are not available for comparison. The tendency to deviate from the rule is likewise shown by the Zr III multiplets representing the transitions $5p \rightarrow 4d$ and $5d \rightarrow 5p$, Tables 7 and 9. The strongest groups are those for which $\Delta L = 0$, although the multiplets for which $\Delta L = \pm 1$ are also prominent in the $5p \rightarrow 4d$ group but much weaker or missing in the $5d \rightarrow 5p$ group. The same effect is noticeable among the corresponding Ti III multiplets. The $5p \rightarrow 5s$ multiplets of Zr III, Table 7, show no marked differences in intensity, whereas in Ti III they conform strictly to the above rule.

[19] Astrophys. J., **66**, p. 13; 1927. [20] Zeit. für Physik, **33**, p. 261; 1925.

VI. CONCLUSION AND ACKNOWLEDGMENTS

The classified lines of Zr IV and Zr III can all be accounted for by means of the terms required theoretically for atomic systems with one and two external electrons. When these lines are stricken from the lists of observed wave lengths there still remain many, mostly faint, of unknown origin. Some may be due to impurities, but it is more probable that the majority of these unclassified lines result from excitation of the outermost electrons of the krypton configuration.

In the course of this work we have received valued assistance from various persons. Again we wish to express our appreciation to Dr. H. C. Rentschler, of the Westinghouse Research Laboratory, for supplying us with metallic Zr electrodes of high purity, and to Dr. K. Burns, of the Allegheny Observatory, who placed his standard ultra-violet Fe wave lengths at our disposal in advance of publication. To Bourdon F. Scribner, of the bureau staff, and to D. D. Laun, formerly of the bureau staff, we are indebted for much assistance with the wave-length observations and calculations. Finally, one of us (R. J. L.) wishes to acknowledge a grant from the Research Council of Canada which has made possible his cooperation in this investigation.

WASHINGTON, April 3, 1930.

PHASE EQUILIBRIA IN THE SYSTEM Cr_2O_3-SiO_2

By E. N. Bunting

ABSTRACT

A study of the phase equilibria in the system Cr_2O_3-SiO_2 has shown that no compounds exist and that the two oxides are practically immiscible in the solid and liquid states. The melting point of Cr_2O_3 was found to be 2,140° ± 25° C.

CONTENTS

	Page
I. Introduction	325
II. General method	325
III. Results	326
IV. The melting point of Cr_2O_3	326
V. Acknowledgments	327

I. INTRODUCTION

Although chrome ores have long been used in the metallurgical and ceramic industries, nothing has been reported on the phase equilibria existing at high temperatures between Cr_2O_3 and the other oxides usually associated with it. Chrome refractories [1] seldom contain more than 60 per cent of Cr_2O_3, since they are made from chromite ($FeO \cdot Cr_2O_3$) ores, which contain, in addition to the FeO present, several per cent of silica, alumina, etc., as impurities. As chrome refractories are often used in contact with silica in furnace construction, the simple binary system of Cr_2O_3 and SiO_2 seemed most appropriate for an initial investigation.

II. GENERAL METHOD

Mixtures of powdered Cr_2O_3 (99.2 per cent) and SiO_2 (99.7 per cent) were prepared in stick form and fused in the oxyhydrogen flame. Repeated grindings and fusions were made to obtain homogeneous mixtures. Small pieces (10 to 20 mg) of the mixtures were placed in the central hole of an Ir-Pt alloy button and heated for an hour or more in an Ajax induction furnace.[2]

Temperatures were measured with a disappearing filament optical pyrometer [3] sighted on the outer hole in the button. The coil of the induction furnace was mounted on a rotatable platform so that it could be inverted to allow the button to drop out into a quenching bath of water. Granular thoria was placed under the button to keep it from sticking in the crucible in which the button was heated. In this quench instantaneous cooling to room temperature was not

[1] McDowell and Robertson, J. Am. Ceram. Soc., 5, p. 865; 1922.
[2] This iridium-button furnace has been described in a previous paper. This Journal, 4, p. 131; 1930.
[3] The pyrometer was calibrated before use by the pyrometry section of this bureau.

obtained, since the button weighed about 50 gm, but a drop in temperature of several hundred degrees took place rapidly enough to prevent any appreciable shift in the equilibrium attained at the high temperature.

The melts were removed from the hole in the button by breaking them up with a pointed hardened steel punch. Mixtures containing not more than a few per cent of Cr_2O_3 were sufficiently transparent to be examined under the microscope. The opaque mixtures were examined by the powder method in the X-ray spectrograph.[4]

In order to obtain a uniform distribution of the Cr_2O_3 in mixtures containing less than 1 per cent of it, a hot-water solution of ammonium silicofluoride and chromium nitrate was treated with excess ammonium hydroxide, giving a precipitate of chromium hydroxide intimately mixed with silicic acid. This precipitate was washed, dried, and fused in stick form in the oxyhydrogen flame.

III. RESULTS

Under the microscope mixtures containing 0.1 per cent or more of Cr_2O_3 and which had been heated to 2,100° C. for an hour showed the presence of undissolved Cr_2O_3 in substantially the same amount as before the heat treatment. The mixture containing 0.1 per cent Cr_2O_3 was colored a light bluish green, the color becoming dark green with higher Cr_2O_3 content. There is probably a slight solubility of Cr_2O_3 in SiO_2, but not enough to determine or to distinguish the eutectic temperature from the melting point of silica. A very slight but undetected solubility of SiO_2 in Cr_2O_3 above 2,140° must also be assumed.

X-ray spectrograms of mixtures containing 92, 86, 71, 57, 43, 29 and 14 per cent by weight of Cr_2O_3, which had been heated for two hours at 1,750° and then quenched, indicated that no compounds were formed and that the only crystals present were of Cr_2O_3.

All mixtures containing more than about 35 weight per cent of Cr_2O_3 had to be heated to over 2,100° C. before becoming noticeably fluid. Quenched mixtures which had been heated in the oxyhydrogen flame above the melting point of Cr_2O_3 showed the presence of two immiscible liquid phases.

IV. THE MELTING POINT OF Cr_2O_3

The melting point of Cr_2O_3 was determined by direct observation on a small piece of prefused Cr_2O_3[5] placed in the Ir-Pt button. The field of view in the pyrometer covered both holes in the button, and when a temperature of 2,140° C. was reached the Cr_2O_3 was seen to melt. Duplicate determinations agreed within 5° C., but the measurements are considered to be accurate only to ±25° C. The pyrometer was used soon after calibration, but, as an additional check, a similar determination was made of the melting point of pure Al_2O_3, which was found to be 2,040° C. This is in good agreement with the value (2,050°) given in the International Critical Tables.

[4] X-ray spectrograms were made by the metallurgical division of this bureau.

[5] This Cr_2O_3 was prepared from C. P. $Cr(NO_3)_3$ by precipitating a hot 1 per cent water solution with pure NH_3 gas. The precipitated $Cr(OH)_3$ was washed, dried, and fused in the oxyhydrogen flame. Analysis by conversion to chromate and titration with KI and thiosulphate gave 99.9 per cent Cr_2O_3. The 99.2 per cent Cr_2O_3 melted at 2,125° C.

All previous observations [6] on the melting point of Cr_2O_3 have been made in carbon resistor electric furnaces in which partial reduction of the Cr_2O_3 may have occurred. Thus, Ruff obtained values ranging from 1,830° to 2,080° C., depending upon the rate of heating and the nature of the gas present in the furnace, and concluded that the true melting point could not be determined in a carbon furnace.

V. ACKNOWLEDGMENTS.

The writer is indebted to E. W. Washburn for suggesting and supervising this work, and to the other members of the bureau whose cooperation was obtained.

WASHINGTON, April 9, 1930.

---

[6] (2,059°) Goecke, Metallurgie, **8**, p. 667; 1911. (2,059°) Ruff and Goecke Z. für angew. Chem., **24**, p. 1911. (2,080°) Ruff, Z. für anorg. Chem., **82**, p. 373; 1913. (1,990°) Kanolt, Bur. Std. Bul., **10**, p. 295; 14.

METHOD OF MEASURING FRICTIONAL COEFFICIENTS OF WALK-WAY MATERIALS

By R. B. Hunter

ABSTRACT

This paper describes apparatus and methods for measuring coefficients of friction of walk-way surface materials. Conditions of the surface which affect the frictional coefficients of walk-way materials are examined, and data illustrating the precision obtainable by the methods described are given and discussed in their relation to the slipping hazard in walk-ways.

CONTENTS

		Page
I.	Introduction	329
II.	Purpose of the investigation	330
III.	Materials investigated	330
IV.	Methods employed	330
V.	Preparation of worn surfaces	331
	1. The wearing apparatus	331
	2. Wearing process	332
VI.	Friction measurements	333
	1. Performance requirements of the apparatus	333
	2. Description of apparatus	333
	3. Friction test values	333
	4. Effect of smoothness of test surfaces	334
	5. Effect of area of contact and pressure between surfaces	334
VII.	Standardization of surface conditions	336
	1. Smoothness of test soles	336
	2. Effect of different leathers	337
	3. Effect of humidity	338
	4. Temperature and humidity control	340
	5. Reproduction of test conditions	341
VIII.	Simulated service conditions	343
	1. Friction measurements under simulated service conditions	343
	2. Test procedure on wet and oily surfaces	344
IX.	Discussion of friction data	346
X.	Summary of conclusions	347

I. INTRODUCTION

Project A–22 of the American Standards Association deals with the formulation of a safety code for walk-way surfaces. The sectional committee, which was organized to prepare this code, found the available data on walk-way surfaces and materials to be inadequate for the satisfactory formulation of a code, and appealed to the manufacturers for assistance in this connection. In response to this request, a manufacturers' subcommittee composed of a large group of manufacturers and distributors of walk-way materials was formed, and arrangements were made in July, 1924, for a research fellowship at the National Bureau of Standards to conduct an experimental investigation of the frictional resistances of walk-way surface materials.

This investigation resulted in the development of an apparatus and process for preparing specimens of walk-way surface materials for friction measurements and an apparatus and methods for measuring coefficients of friction. A report of the investigation was submitted to the manufacturers' subcommittee in July, 1926.

Because of the incompleteness of the research it seemed advisable for the Bureau of Standards to conduct a further independent investigation of the problem, which was made by the former research associate in 1928 and 1929.

II. PURPOSE OF THE INVESTIGATION

The purposes of the original investigation were to develop a satisfactory method for measuring the frictional resistances of walk-way materials and to obtain data to aid the sectional committee in the formulation of a walk-ways safety code. The purposes of this paper are to describe the apparatus and methods developed in the earlier research, to review after the lapse of considerable time the data and the methods originally employed, and to examine these data as to their usefulness as a basis of evaluating the effectiveness of various materials in relation to the walk-ways safety problem.

III. MATERIALS INVESTIGATED

In the investigations of 1924–1926, friction measurements under different conditions were made on 148 specimens of walk-way and flooring materials. Specimens of most of the materials extensively used, as well as many less commonly employed in walk-way or floor surfaces, were included in this list. Twenty-four specimens, covering extreme ranges in hardness, smoothness, compressibility, absorptive power, and other characteristics affecting the coefficient of friction were chosen from these for the 1928–1929 investigation. In some cases two or more specimens of the same or of allied materials were chosen to afford a closer study of their coefficients of friction.

Each of the 24 specimens is designated in the tables by a letter. These materials are roughly grouped according to their origin and physical characteristics as follows: Specimens C, D, E, F, G, I, and J are smooth-faced natural stone products, such as slate, marble, and travertine, with the exception of one specimen of vitrified tile; specimens Q, R, and S are wood, including smooth maple, larch, and yellow pine flooring; specimens T, W, P, and U are artificial stone products, some containing hard abrasive in the mixture; specimens A, B, H, and K are smooth-faced somewhat compressible manufactured products, such as rubber, cork carpet, and linoleum; specimens L, M, N, O, and V are metal products having ridged or otherwise roughened surfaces, some containing embedded hard abrasive and others presenting a clear metal surface.

IV. METHODS EMPLOYED

The safety or the slipping hazard offered by any given walk-way surface at a given time depends among other factors on the friction between the shoe sole and the walk-way surface at that time. The coefficient of friction is a direct measure of the resistance to slipping

The coefficient of friction is defined as the ratio of the force, F, required to slide one surface on the other, to the force, F', pressing the two surfaces together, or F/F'. When F is the force required to start the motion, F/F' is the static coefficient of friction; and when F is the force required to maintain a uniform motion, F/F' is the kinetic or dynamic coefficient of friction. In general, the static friction is the greater. The kinetic friction on some materials increases considerably with the velocity and may be greater than the static friction.

The law of friction may be stated as follows: The coefficient of friction between two given surfaces is a constant which is independent (within limits) of the area of contact and the force pressing the surfaces together. It is to be understood, however, that this constant applies only to two given surfaces. Another coefficient of friction may be obtained with other surfaces of the same materials.

There are a number of variable conditions which affect the coefficient of friction between a shoe sole and a walk-way surface—the smoothness of the shoe sole and the walk-way surface, the dryness of the two surfaces, and the presence of other substances between the two surfaces, as dirt, water, oil, etc. It consequently seemed advisable to measure the coefficients of friction of a variety of walk-way surface materials (1) under a standard or controlled surface condition and (2) under surface conditions simulating as nearly as possible actual service conditions, as a basis for determining the usefulness of friction measurements under controlled conditions.

For this purpose coefficients of friction were measured as follows: (1) Between clean, dry, oak-tanned leather soles and clean, dry, worn specimens of the walk-way materials; (2) between clean, wet, oak-tanned leather soles and clean, wet, worn specimens of the walk way materials; (3) between dirty, wet, worn specimens of the walk-way materials and (*a*) dirty, wet, oak-tanned leather soles and (*b*) dirty, wet, rubber soles; and (4) between oily, worn specimens of the walk-way materials and (*a*) oily, oak-tanned, leather soles and (*b*) oily rubber soles.

V. PREPARATION OF WORN SURFACES

It became evident from an examination of the surfaces of both new and service-worn specimens that friction measurements on new or unworn specimens of walk-way materials would give little indication of the relative antislip values of the materials in actual service. Some materials become smoother and some rougher under footwear. Measurements on the worn surfaces are therefore essential.

The time required to secure service-worn specimens and the uncertainty regarding their definite identification if taken from an old walk way render any attempt to obtain service-worn specimens for general tests impractical. An apparatus and process for producing accelerated wear in the laboratory are therefore essential.

1. THE WEARING APPARATUS

The apparatus shown in Figure 1 was constructed after preliminary tests with different abrasives and processes. It consists of a motor-driven reciprocating arm carrying two square frames into which leather-soled, weighted shoes are loosely fitted. By means of a

ratchet the shoes are slowly rotated. The reciprocating arm mak 34 transits per minute, and the shoes one complete revolution in transits. The resultant motion is a slide and twist with a slig rocking motion of the shoe on the walk-way surface with each strok Dry sand (50 to 100 mesh) is fed slowly through two holes in ea shoe, 4 inches apart. The rotation tends to keep the sand even distributed and to prevent scoring. It will be observed that wh 50 to 100 mesh sand is fed continuously into the machine, the actu abrasive between the surfaces has somewhat different properti The sand remains between the wearing surfaces for a time, becom worn and crushed in the process, and mixes with the particles wo from the surfaces. The actual abrasive in use at any time is mixture of fresh and crushed sand and dust from the sand, leath sole, and the walk-way material. Owing to the dust formed, it advisable to have the abrasive machine inclosed in a dust-tig compartment with the motor and reducing gear outside.

2. WEARING PROCESS

The wearing process to which the walk-way materials were su jected may be divided into three parts:

1. All specimens were subjected to periods of wear with the abr sive described such that the surfaces were abraded by approximate equal amounts (about one-sixteenth inch in depth). Depending the resistance of the materials to abrasion, these periods of we varied from 10,000 to 80,000 transits of the shoe. Each specimen w rotated through 180° in the middle of the process to insure mo uniform wear.

2. Following part 1, the sand feed was removed and the sa and dirt wiped from the specimen and the shoe. The specime were then subjected uniformly to 1,000 transits of the shoe witho any abrasive. Each specimen was again rotated through 180° in t middle of the process.

3. The specimens were then cleaned and finished by hand, follows: They were washed under running water, wiping alternate with a wet cloth and the beveled edge of a picee of chrome-tanne sole leather to remove any embedded sand and encrusted dirt. The were then dried, and when thoroughly dry were dressed by rubbi first with a piece of No. 1½ sandpaper, then with a piece of No. sandpaper. About 25 strokes in each of two directions at rig angles with the sandpaper held on the open palm of the hand we given to each specimen with each kind of sandpaper. Finall immediately before the friction measurement the specimen w rubbed in each of two directions with the beveled edge of a piece oak-tanned sole leather and wiped with a dry cloth.

Trial specimens of several walk-way materials were prepared b these processes and compared with service-worn specimens of t same material by means of friction measurements. Some of the friction measurements are given in Table 1. It will be observe that when the coefficient of friction of the service-worn and labor tory-worn specimens are compared with that of the unworn specim the change is usually comparable in amount. This is believed to b the criterion by which the suitableness of the process should b judged. These seven materials cover extreme ranges in hardnes

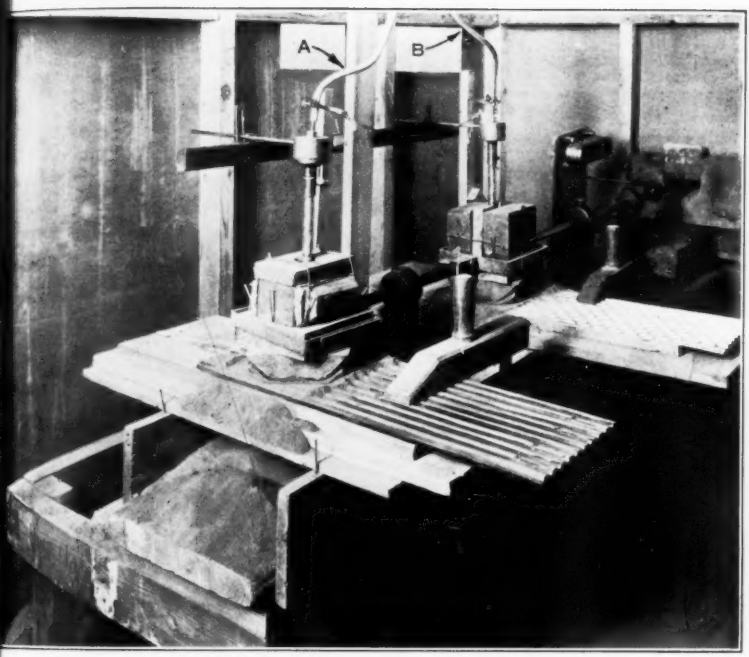


FIGURE 1.—*Apparatus for preparing worn specimens*

A and B, rubber tubes leading to sand hopper.

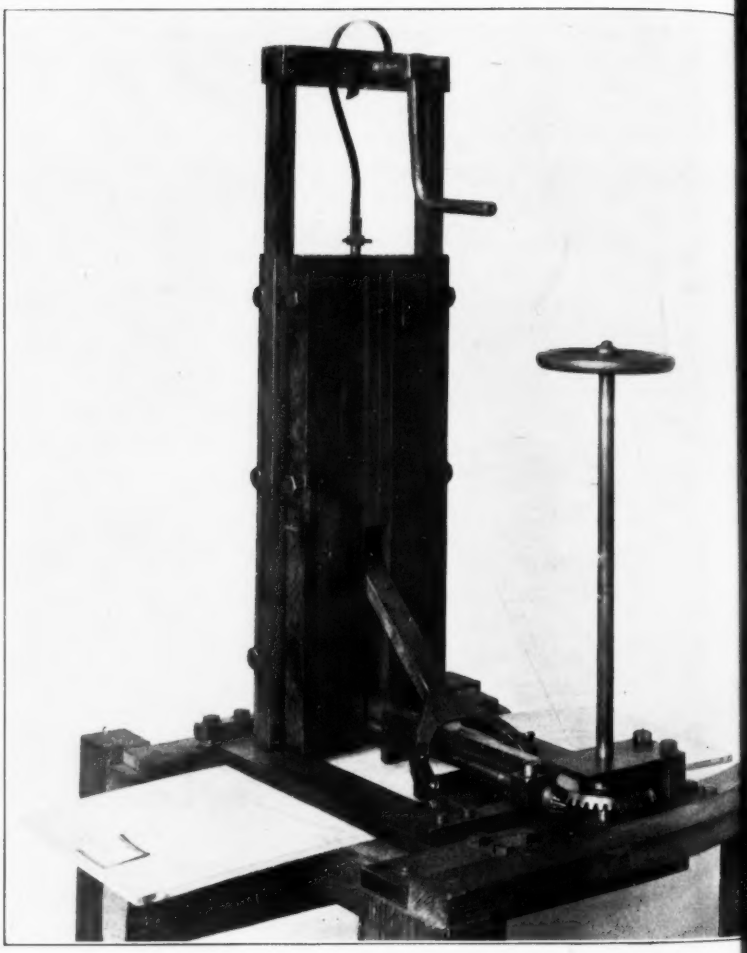


FIGURE 2.—*Friction measuring apparatus*

oughened surface contour, etc. The service-worn specimens were repared for the test by washing, wiping with a cloth, and drying.

ABLE 1.—*Friction measurements on service-worn and laboratory-worn specimens*

aterial No.	Coefficients of friction			Material No.	Coefficients of friction		
	On unworn specimen	On laboratory-worn specimen	On service-worn specimen		On unworn specimen	On laboratory-worn specimen	On service-worn specimen
.....	0.24	0.29	0.24	5.....	0.48	0.36	0.30
.....	.55	.29	.35	6.....	.42	.28	.26
.....	.48	.31	.30	7.....	.23	.18	.20
.....	.45	.29	.27				

VI. FRICTION MEASUREMENTS

1. PERFORMANCE REQUIREMENTS OF THE APPARATUS

Friction-measuring apparatus for walk-way materials should nbody the following features:

1. It should be adapted to measurements on relatively small areas, avoid the necessity of preparing large worn surfaces.
2. The contact area between the surfaces should be comparable the contact area between an average shoe sole and a walk way.
3. The standard load applied to the test sole should approximate e mean load applied to the shoe sole in walking.
4. The apparatus should be capable of duplicating measurements the friction between unchanging surfaces.

2. DESCRIPTION OF APPARATUS

The apparatus shown in Figure 2 is simple in construction and anipulation and is believed to meet the peformance requirements umerated. It operates on an oblique thrust principle correspond- g to the thrust on the shoe in walking and consists of a right-angled ame carrying a slotted 75-pound weight between two vertical bars the frame which serve as guides to the weight. A 10-inch thrust m is pivoted at one end near the center of gravity of the weight and the other end through the center of area of a 3 by 3 inch shoe. he weight may be raised by means of the windlass, and is supported the raised position by the friction of the shoe on the surface under st. By means of a screw and lug the shoe may be drawn forward by nall increments, increasing the horizontal component of the force til the shoe slips on the surface, letting the weight drop. The lug left in the position at which the slip occurred. The lug carries an dex which shows (on a scale graduated in inches) the horizontal stance of the shoe from its position when the thrust arm is vertical. his scale may be graduated to read in coefficients of friction directly desired.

3. FRICTION TEST VALUES

The coefficient of friction is derived from the scale reading and the mension of the apparatus. The vertical force, F' and the horizontal rce F acting on the shoe in any position are equal, respectively, to

the vertical and horizontal components of the thrust transmitted t the shoe. In this case the coefficient of friction, or the ratio F/F', equal to the tangent of the angle the thrust arm makes with the verti cal at the point of slipping. The sine of this angle is one-tenth of th scale reading in inches. The tangent of the angle—that is, the coeffi cient of friction—may be obtained from a table of natural sines an tangents, or a table giving the coefficient of friction corresponding t any scale reading may be readily constructed. In making th measurements which follow, the reading on the scale graduated i 0.05-inch divisions was taken to the nearest scale division, and th corresponding natural tangent representing the coefficient of frictio was recorded to the nearest 0 or 5 in the third decimal place.

4. EFFECT OF SMOOTHNESS OF THE TEST SURFACES

The data in Table 2 were obtained from specimens freshly dresse but not rubbed with oak-tanned sole leather as previously describe for the final dressing process. Twelve measurements were made o each specimen without redressing either the walk-way specimen or th test sole. It will be observed that when repeated measurements o the same specimen are thus made there is a continuous and fairl regular decrease in the coefficient of friction tending toward a constan minimum value. This decrease is evidently due to the smoothin of either the surface of the specimen or the surface of the test sole o both. For this reason a final dressing of the walk-way surface wit leather and a standard preparation of the test sole is advised befor beginning the friction measurements.

TABLE 2.—*Typical values for repeated measurements*

Measurement No.	Coefficients of friction				
	Leather on leather	Leather on C	Leather on J	Leather on L	Leath on V
Initial	0.380	0.270	0.480	0.195	0.
2	.355	.220	.425	.170	.
3	.350	.200	.405	.160	.
4	.345	.190	.385	.155	.
5	.335	.185	.375	.150	.
6	.330	.180	.365	.145	.
7	.330	.175	.365	.140	.
8	.325	.170	.360	.140	.
9	.325	.165	.360	.140	.
10	.320	.165	.360	.140	.
11	.320	.160	.360	.140	.
12	.320	.160	.360	.140	.

5. EFFECT OF AREA OF CONTACT AND PRESSURE BETWEEN SURFACES

While the law of friction states that the coefficient of friction between the same two surfaces is independent of the area of contact and the force pressing the surfaces together, some variation may be expected if these factors vary widely, and marked compression or abrasion of the materials occurs. The data in Tables 3 and 4 show that errors due to changes in area and load are negligible in comparison

with other unavoidable discrepancies in measuring the coefficient of friction of walk-way materials. In Table 3 the first three measurements on each specimen were made with the standard 75-pound weight in the apparatus, the second three with the weight increased to 150 pounds, and the last three with the standard weight. The specimens were dressed for each series by the standard process described earlier and the sole for each series by a standard process later described. Each series of nine measurements on the same specimen was made without redressing or removing the specimen or shoe from the apparatus. In Table 4 the first three measurements were made with a standard 3 by 3 inch (9 square inches) sole, the second three with the same sole reduced to 1.5 by 3 inch (4.5 square inches) by cutting a strip from each side, and the last three with the sole again increased to standard size by replacing the strips. The sole and each specimen were redressed before each series of nine measurements as in Table 3. These four specimens were the same as used in Table 2 and represent for walk-way materials extreme ranges in hardness, compressibility, and roughness of surface.

TABLE 3.—*Effect of weight*

Measurement No.	Weight on shoe	Area of shoe	Pressure	Coefficient of friction leather on specimen—			
				C	J	L	V
	Pound	*Square inches*	*Lbs./in.²*				
Initial	75	9	8.3	0.210	0.410	0.170	0.315
	75	9	8.3	.200	.390	.155	.290
	75	9	8.3	.195	.385	.150	.285
	150	9	16.7	.190	.365	.145	.295
	150	9	16.7	.175	.360	.145	.295
	150	9	16.7	.170	.355	.145	.290
	75	9	8.3	.185	.355	.145	.290
	75	9	8.3	.185	.355	.145	.285
	75	9	8.3	.185	.355	.145	.280

TABLE 4.—*Effect of area of contact*

Measurement No.	Weight on shoe	Area of shoe	Pressure	Coefficient of friction leather on specimen—			
				C	J	L	V
	Pound	*Square inches*	*Lbs./in.²*				
Initial	75	9	8.3	0.230	0.425	0.175	0.320
	75	9	8.3	.210	.405	.160	.295
	75	9	8.3	.195	.390	.155	.275
	75	4.5	16.7	.195	.395	.155	.275
	75	4.5	16.7	.190	.390	.150	.275
	75	4.5	16.7	.190	.385	.145	.275
	75	9	8.3	.190	.385	.145	.290
	75	9	8.3	.190	.375	.145	.285
	75	9	8.3	.190	.375	.145	.280

Comparing these data with the data of Table 2, it will be observed that the decrease in the coefficient of friction with varying weight or area of sole is almost as regular as with constant weight and constant

area of sole, and that if the initial readings in Table 2 are discarde there is a fairly close agreement. The area of contact and the pressu do have some effect on the coefficient of friction when compressi and abrasion are factors, but the effect is negligible in comparis with the variations due to other causes, such as the inability reproduce surface conditions.

VII. STANDARDIZATION OF SURFACE CONDITIONS

We have stated that smoothness, cleanness, and dryness are facto that affect the value of the coefficients of friction between two su faces, and therefore it is necessary to standardize the test surfaces respect to these factors in order to obtain results reproducible another time with any degree of precision. This applies to both su faces, the surface of the sole as well as the surface of the specimen.

Smoothness is a relative term. It is difficult to define exact degre of smoothness and to reproduce them for standard tests. Coefficien of friction measured on relatively smooth surfaces will be more co sistent than those measured on rougher surfaces.

The process previously described for preparing specimens for fri tion measurements does not exactly reproduce the same degree smoothness even in the same walk-way material, but no better mea has been discovered or proposed. The smoothness of the test s can be standardized to a greater degree than that of the walk-w specimen. The test sole may be dressed by a standard process un it gives a selected standard coefficient of friction between it a another surface of the same material as the test sole.

1. SMOOTHNESS OF TEST SOLES

The standard adopted for oak-tanned leather soles in these measur ments was obtained by dressing the leather sole on a piece of No. sandpaper until a comparatively smooth, velvety surface was pr sented. Another piece of the leather, about 8 by 10 inches, w dressed in the same manner. The test sole was then operated in t friction-measuring apparatus until an approximately constant val of the coefficient of friction, 0.310, between leather and leather w obtained. The number of operations in the friction apparatus r quired to reach 0.310, the value of the coefficient of friction selecte as indicating standard smoothness, depends on the smoothness of t initial dressing and apparently to some extent on the temperature a humidity.

The data in Table 5 give the coefficients of friction obtained successive operations in typical runs in reducing the test sole standard smoothness at different temperatures and relative humi ties. In addition to the data for individual runs, the average initi readings and the average number of operations in the friction-measu ing apparatus required to reach standard smoothness in 10 dressin of the sole are given.

TABLE 5.—*Coefficients of friction leather on leather obtained in reducing test soles to standard smoothness*

Readings	Temperature, °F.				
	65	80	65	80	85
	Relative humidity (per cent)				
	45	45	80	80	85
	Humidity (in grams per cubic foot)				
	3.1	4.9	5.4	8.8	10.8
	Coefficient of friction				
Initial	0.375	0.365	0.360	0.355	0.355
	.355	.350	.345	.335	.335
	.345	.340	.335	.325	.330
	.335	.335	.330	.320	.325
	.330	.330	.325	.320	.320
	.330	.330	.325	.315	.320
	.325	.325	.320	.315	.315
	.325	.325	.320	.315	.318
	.320	.320	.315	.310	.315
	.320	.320	.315		.310
	.320	.320	.315		
	.320	.315	.315		
	.315	.315	.310		
	.315	.315			
	.315	.310			
	.315				
	.315				
	.310				
Average initial reading of 10 series	.376	.372	.364	.359	.354
Average number operations to reach 0.310, 10 series	18.1	16.1	10.3	7.6	6.4

It is interesting to note that in these data the coefficient of friction tween leather and leather apparently decreases with increase in solute humidity. This is indicated both by the decrease in the efficient of friction in the initial operation and by the decrease in e number of operations required to reach a value of 0.310, as the solute humidity increases. This is exactly opposite to the effect humidity on the coefficients of friction between leather and most alk-way materials.

The process just described was employed in all later measurements der dry conditions unless otherwise stated, and the test sole was nsidered to have reached the standard condition of smoothness hen the first reading giving a value of 0.310 for the coefficient of ction of leather on leather was reached. While it does not insure absolute standard of smoothness it is the best method discovered.

2. EFFECT OF DIFFERENT LEATHERS

The data in Table 6 illustrate the variation in the standard sole at may be expected due to the use of different test soles. Sole 4 as a clear firm piece of oak-tanned sole leather in excellent condi-on; sole 1 was a firm, clear piece of oak-tanned sole leather worn in

tests until it showed a slightly hardened spot on one edge; sole 2 w a firm, clear piece of oak-tanned sole leather which had been worn tests until it resisted the prescribed velvety finish; and sole 3 was clear piece of oak-tanned sole leather slightly flanky in appearan and slightly worn in previous tests. These measurements were ma at 70 ± 2° F. and a relative humidity of 65 ± 2 per cent. The wal way specimens had been stored in the laboratory for about two yea after they had been dressed for the previous tests. They were washe cleaned, and dried for these measurements, but their surface were not redressed, and for this reason some of the specimens gi coefficients of friction higher or lower than obtained on the sa specimen when freshly dressed by the standard process. The sol were freshly dressed and brought to standard smoothness for ea test. The measurements were made on each specimen from left right as recorded, and only one measurement with each sole was ma on the same specimen in order to avoid the smoothing effect of r peated measurements. For this reason the values are higher th the average when a series of several tests are made on the same spe men without redressing the specimen and sole.

TABLE 6.—*Effect of different leathers*

Specimen	Coefficients of friction with sole				
	No. 4	No. 1	No. 2	No. 3	No.
J	0.405	0.410	0.435	0.420	0.
A	.310	.310	.310	.315	.
C	.215	.210	.225	.230	.
L	.220	.215	.225	.210	.
G	.245	.240	.255	.245	.
P	.295	.285	.325	.290	.
Q	.460	.455	.435	.450	.
O	.450	.505	.475	.460	.
U	.485	.485	.490	.465	.

The duplicate measurements made on the same specimen with t same piece of leather (sole 4) differ from the mean by amounts var ing from 0 to about 5 per cent. Of the 27 measurements made wi soles 1, 2, and 3 only two measurements show a greater differen and these two were obtained with soles which had been previous rejected as standard because of obvious defects. It therefore see reasonable to assume that if the soles are carefully selected from fir clear pieces of leather the differences in the frictional properties oak-tanned sole leathers are negligible in comparison with the m chanical differences in the smoothness of the surface obtainable by standard process of dressing.

3. EFFECT OF HUMIDITY

The effect of temperature and relative humidity or of absol humidity on the coefficient of friction has been pointed out. T data in Table 7 show the variation in the coefficient of friction whi may occur on clean dry walk-way surfaces due to ordinary atm pheric changes in temperature and humidity in the interior of buil ings. These measurements were taken in the order of increasi

absolute humidity without redressing the walk-way specimen. The sole was redressed and brought to the standard value, 0.31 (leather on leather) before each measurement.

TABLE 7.—*Variation in coefficients of friction with temperature and humidity*

Specimen	Temperature (°F.)				
	65	80	65	80	85
	Humidity (per cent)				
	45	45	80	80	85
	Humidity (in grams per cubic foot)				
	3.1	4.9	5.4	8.8	10.8
	Increase in moisture (per cent)				
	----------	61	78	187	258
	Coefficients of friction				
J	0.445	0.450	0.485	0.435	0.430
H	.325	.345	.355	.410	.495
A	.290	.315	.320	.355	.505
B	.305	.330	.345	.375	.455
C	.210	.215	.225	.240	.280
D	.195	.205	.310	.225	.285
E	.195	.200	.210	.265	.290
F	.195	.200	.210	.230	.255
N	.160	.165	.170	.195	.230
I	.295	.315	.320	.320	.360
W	.200	.215	.245	.265	.275
P	.315	.285	.320	.340	.390
O	.275	.260	.285	.310	.365
M	.275	.260	.305	.315	.340
L	.225	.235	.250	.285	.315
T	.225	.245	.255	.305	.385
G	.235	.235	.260	.285	.315
Q	.295	.295	.320	.290	.295

Of these specimens all except two show a marked increase in the coefficients of friction with increase in the absolute humidity. The two exceptions—one rubber tile and one wood flooring—show some indication of the opposite effect which, however, may be partly due to the smoothing effect of repeated measurements.

The measurements were made from left to right on each specimen without redressing it, in order to avoid erratic changes. Table 8 gives data for 5 specimens, 2 of rubber tile and 3 of wood, in which the measurements were made (*a*) from left to right as before in the order of increasing humidity, and (*b*) from right to left in the order of decreasing humidity, all without redressing the specimen. The mean of the two measurements at the same temperature and humidity should at least partially eliminate or average the smoothing effect. These rubber specimens were rubbed to a smoother finish than for the previous measurements of Table 7 and for that reason the coefficients of friction in Table 8 are generally lower.

TABLE 8.—*Effect of temperature and humidity*

Specimen	Temperature (°F.)				
	65	80	65	80	85
	Humidity (per cent)				
	45	45	80	80	85
	Coefficients of friction				
J (*a*)	0.325	0.345	0.325	0.320	0.6
J (*b*)	.345	.325	.320	.285	.7
Mean	.335	.335	.322	.302	.6
K (*a*)	.375	.365	.350	.335	.5
K (*b*)	.350	.320	.290	.290	.3
Mean	.362	.342	.320	.312	.4
Q (*a*)	.295	.295	.320	.290	.3
Q (*b*)	.290	.285	.280	.285	.3
Mean	.292	.290	.300	.287	.3
R (*a*)	.320	.345	.350	.350	.3
R (*b*)	.345	.335	.325	.335	.3
Mean	.332	.340	.337	.342	.3
S (*a*)	.290	.305	.320	.305	.3
S (*b*)	.295	.280	.270	.280	.2
Mean	.292	.292	.295	.292	.2

Judging from the data in Tables 7 and 8 there is no regular increas or decrease in the coefficients of friction of such materials as rubbe and wood with increasing humidity.

There is one marked difference in the data on rubber in Tables and 8 which is worthy of note and comment. It will be observed i Table 8 there is an abrupt rise in the coefficients of friction at 85° F and 85 per cent relative humidity, more marked on specimen J tha on specimen K, which is not shown in the data of Table 7. This probably due to a softening of the material under those condition In fact, specimen J had a sticky feeling when the exceptionally hig coefficients of friction were obtained. Other measurements made o specimens of rubber at the same and higher temperatures and humid ties gave the same kind of erratic results.

There is no apparent explanation for this change in friction wit change in humidity, and speculation regarding it seems to lead to n definite conclusion. Similar phenomena are observed in the behavi of brake bands, belts, and such devices in which the efficiency o operation depends on friction. The data show clearly, however, th necessity of controlling the temperature and humidity within rath narrow limits of variation, if reproducible values of the coefficient o friction are to be obtained.

4. TEMPERATURE AND HUMIDITY CONTROL

The data in the preceding Tables 7 and 8 and in Tables 9 and following were made in a chamber in which the temperature w held constant within ±2° F. and the relative humidity within ±

per cent of the desired selected conditions. The walk-way specimens and the test soles were stored under each selected condition for at least four hours before the measurements were made. No regular change was detected in the coefficients of friction of any material taken from relatively dry storage and stored for that length of time under standard conditions, and four hours is believed to be sufficient time in which to attain a fairly constant condition in the surface layer.

5. REPRODUCTION OF TEST CONDITIONS

The data in Table 9 indicate the probable precision in friction measurements attainable by the methods described. These measurements were made on specimens prepared by the standard process previously described. Each specimen was subjected to part 3 of the process, hand dressing, immediately before starting each series of measurements. The sole was redressed and brought to the selected standard coefficient of friction of 0.31 on leather immediately before each series. Five successive measurements were made in each series without redressing the specimen or sole. All measurements were made at $70° \pm 2°$ F. and 65 ± 2 per cent relative humidity after the sole and specimen had been stored for at least four hours under that condition. The average for each series and the general average of these for each material are given.

TABLE 9.—*Friction measurements at $70° \pm 2°$F. and relative humidity of $65+2$ per cent*

Specimen	Reading	Coefficients of friction				
		Series 1	Series 2	Series 3	Series 4	General average
	1	0.205	0.195	0.195	0.205	
	2	.170	.170	.165	.180	
	3	.165	.160	.155	.165	
	4	.160	.155	.150	.165	
	5	.160	.155	.150	.160	
Average		.172	.167	.163	.175	0.169
	1	.205	.200	.205	.200	
	2	.170	.165	.170	.170	
	3	.160	.165	.160	.160	
	4	.155	.165	.160	.160	
	5	.150	.165	.160	.160	
Average		.168	.172	.171	.169	.170
	1	.190	.170	.140	.145	
	2	.160	.135	.135	.135	
	3	.140	.125	.130	.130	
	4	.135	.125	.130	.130	
	5	.135	.125	.130	.130	
Average		.154	.136	.133	.134	139
	1	.180	.175	.195	.175	
	2	.155	.160	.160	.155	
	3	.140	.155	.150	.145	
	4	.135	.150	.145	.135	
	5	.130	.140	.145	.130	
Average		.148	.156	.159	.148	.153
	1	.265	.265	.265	.250	
	2	.245	.245	.250	.245	
	3	.240	.240	.250	.235	
	4	.235	.240	.240	.230	
	5	.235	.230	.235	.230	
Average		.244	.245	.248	.238	.244

TABLE 9.—*Friction measurements at 70° ± 2° F. and relative humidity of 65+ per cent*—Continued

Specimen	Reading	Coefficient of friction				
		Series 1	Series 2	Series 3	Series 4	General average
A	1	0.275	0.270	0.280	0.285	
A	2	.270	.270	.270	.280	
A	3	.265	.270	.270	.280	
A	4	.265	.270	.270	.280	
A	5	.265	.270	.270	.280	
Average		.268	.270	.272	.281	0.27
J	1	.435	.440	.450	.425	
J	2	.405	.400	.405	.375	
J	3	.390	.380	.385	.355	
J	4	.385	.365	.375	.345	
J	5	.385	.365	.365	.335	
Average		.400	.388	.396	.367	.38
U	1	.415	.450	.450	.440	
U	2	.380	.385	.395	.390	
U	3	.360	.365	.370	.360	
U	4	.360	.350	.365	.350	
U	5	.350	.345	.360	.345	
Average		.373	.379	.388	.377	.37
V	1	.340	.385	.360	.355	
V	2	.295	.330	.310	.310	
V	3	.280	.300	.290	.290	
V	4	.270	.285	.285	.270	
V	5	.265	.275	.280	.270	
Average		.290	.317	.305	.300	.30

No attempt is made to predict from these data what precision can be obtained in standardized commercial friction tests on walk-way surface materials. Some indication of the agreement possible is given by a comparison of the measurements recorded in Table 9 with measurements made on the same specimens in 1926. (See Table 10.)

Specimens L and N are omitted from Table 10. The worn surfaces of these specimens were slightly coated with an oxidized film in 1926 which had been removed in redressing them for the 1928 measurements, and for this reason the surfaces are not considered comparable. Since only three measurements were made on each of the specimens in 1926, the averages given for the 1928 measurements in Table 10 are for the first three measurements in each series.

TABLE 10.—*1926 and 1928 friction measurements*

Specimen	Average coefficents of friction, 1928					Average 1926
	Series 1	Series 2	Series 3	Series 4	Grand average, 1928	
X	0.180	0.175	0.173	0.183	0.178	0.2
C	.178	.174	.178	.183	.181	.2
Q	.250	.250	.255	.243	.250	.2
A	.270	.270	.273	.283	.274	.2
J	.410	.407	.413	.385	.403	.4
U	.385	.400	.405	.397	.397	.3
V	.305	.338	.320	.318	.320	.2

While the averages of the 1926 and 1928 measurements are not strictly comparable, since there was only one series of three measurements on each specimen in 1926 and four series of three measurements each in 1928, they give the only information available as to what agreement may be expected in the results of tests made at different times. Considering that in commercial tests different specimens of each material and different observers will be employed, as close an agreement can not be expected, unless the method is further developed and standardized.

VIII. SIMULATED SERVICE CONDITIONS

There is no direct relation between the coefficients of friction on clean, dry surfaces and on the same materials under various actual service conditions. Few, if any, walk-way materials are dangerously slippery when clean and dry, but walk-way surfaces in actual use are not clean in the sense the term has been employed in this paper and are subject to ordinary atmospheric changes in humidity.

It is common experience that combinations of dirt and water or other fluids make some walk-way surfaces slippery. There is no evidence that any particular combination of dirt and water produces the most slippery surface alike on all walk ways or even on those most easily affected by such conditions. Consequently, there seems to be no possibility of selecting a single or even a limited number of actual service conditions which would adequately represent the various possible conditions on walk-way surfaces and which could be defined and accurately reproduced.

The only practical procedure seems to be to produce simulated service conditions by some selected or standard process and to measure and compare the coefficients of friction given by such surfaces.

1. FRICTION MEASUREMENTS UNDER SIMULATED SERVICE CONDITIONS

The measurements recorded in Tables 11 to 13, inclusive, were obtained in 1926. These data are for specimens for which other data are given in preceding tables, and were selected as covering extreme ranges of roughness, hardness, and compressibility and as being fairly representative of general results obtained for wet and oily surfaces.

For the measurements on clean, wet surfaces the worn part of the specimen was wiped with a saturated cloth until a film of water stood over the entire worn surface. The specimen was then clamped in the apparatus and the friction measurement immediately made.

For the measurements on dirty, wet surfaces the same worn specimens were used and prepared as follows: A bag formed of four ply of cheesecloth was filled with the dust worn from the walk-way materials and leather in preparing the worn specimens, immersed in a vessel of water and worked about until a distinct residue formed in the bottom of the vessel. The worn part of the specimen and the test sole were then treated with the saturated bag lifted from the dirty water, as described for the clean, wet measurements.

For measurements on oil surfaces the specimens and soles were prepared in the same manner as for the measurements on clean, wet surfaces except that oil (medium Polarine) was used in place of water.

For all measurements the test soles were prepared in the same manner as for measurements on dry surfaces up to the point of applying the water or oil, as the case might be. Immediately before the measurement on the specimen the sole was saturated with water or oil and passed over a piece of the same material as the sole, wet or oiled in the same manner as the test specimen and the sole.

The results of the friction measurements indicate that these processes do not produce the same surface conditions, even on the same specimens, but no better method has been discovered or suggested.

2. TEST PROCEDURE ON WET AND OILY SURFACES

It was observed when the coefficients of friction on wet or oily surfaces were measured that if the measurement was made as specified for a dry surface, a much higher value of the coefficient of friction would usually be obtained than on a clean, dry surface. This is especially marked on smooth-faced plane surfaces. It is less marked on ridged or otherwise roughened surfaces. A similar effect may be observed in walking over some wet surfaces. Frequently difficulty is experienced in obtaining a foothold in walking over a wet surface, but after firm contact between the shoe sole and the walk-way surface is made there is less tendency to slip than on a dry surface of the same material.

The apparently abnormally high values of coefficients of friction under these conditions may not be due to an actual increase in friction. They may be explained on the assumption that perfect contact is made and that a seal is formed between the wet or oily surfaces, giving the effect of a partial vacuum under the shoe. If this is the case, the load produced by the difference in pressure is added to the vertical component of the thrust on the shoe, while the horizontal force remains equal to the horizontal component of the thrust. The true coefficient of friction would then be given by the ratio $\frac{F}{F'+(A\times P)}$ in which F is the horizontal and F' the vertical component of the thrust due to the 75-pound weight, A is the area of contact in square inches, and P is the differential pressure in pounds per square inch. The apparent coefficient as measured is F/F'. There seems to be no way to avoid or definitely correct the error, as there is no means of determining how perfect a seal is formed or over what area perfect contact is made. However, if some means of evaluating A and P, or the product $A\times P$, can be discovered, the corrected measurements and those on dry surfaces would have a similar significance, and they would have a much greater value in correlating laboratory measurements with actual service conditions than the uncorrected measurements.

Because of this obvious error, a double measurement was made on all wet and oily surfaces—(*a*) An attempt to measure the difficulty of obtaining a foothold, and (*b*) a measure of the coefficient of friction in the usual manner as on a dry surface. Measurement (*a*) was obtained by raising the weight by increments of about 0.05 of an inch on the horizontal scale and partially releasing it after each increment until a position was reached where the shoe would grip the surface of the specimen and hold the weight. The lug was then

moved to make contact with the shoe and its position recorded. The weight was then fully raised and the measurement (*b*) taken.

Tables 11 to 13, inclusive, give data obtained in 1926 by the methods just described. Table 14 is a comparison of results from measurements made in 1926 with measurements made on the same specimens in 1929.

TABLE 11.—*Coefficients of friction on clean, wet surface materials*

Material	Coefficient of friction			
	1	2	3	Average
(a)	0.780	0.770	0.760	0.770
(b)	.790	.770	.695	.752
(a)	.350	.220	.230	.267
(b)	.640	.625	.630	.632
(a)	.560	.560	.590	.570
(b)	.740	.720	.750	.737
(a)	.750	.640	.610	.667
(b)	.820	.790	.770	.793
(a)	.810	.830	.855	.832
(b)	.855	.880	.865	.867

TABLE 12.—*Coefficients of friction on wet, dirty surfaces*

Material	Coefficient of friction							
	With leather sole				With rubber sole			
	1	2	3	Average	1	2	3	Average
(a)	0.475	0.430	0.375	0.427	0.355	0.355	0.475	0.395
(b)	.525	.485	.490	.500	.570	.640	.660	.623
(a)	.325	.325	.330	.327	.340	.385	.325	.348
(b)	.475	.450	.460	.462	.560	.625	.585	.590
(a)	.545	.525	.530	.533	.660	.650	.635	.648
(b)	.590	.585	.585	.587	.995	.995	.995	.995
(a)	.360	.385	.380	.375	.345	.370	.385	.367
(b)	.460	.505	.525	.497	.585	.585	.585	.585
(a)	.820	.790	.800	.803	.710	.675	.675	.687
(b)	.845	.820	.810	.825	.750	.770	.750	.757

TABLE 13.—*Coefficients of friction on oily surfaces*

Material	Coefficients of friction							
	With leather sole				With rubber sole			
	1	2	3	Average	1	2	3	Average
(a)	0.200	0.265	0.300	0.255	0.270	0.300	0.315	0.295
(b)	.215	.215	.225	.218	.375	.350	.330	.352
(a)	.090	.090	.090	.090	.120	.140	.145	.135
(b)	.100	.100	.100	.100	.215	.200	.200	.205
(a)	.185	.180	.165	.177	.205	.225	.225	.218
(b)	.305	.295	.205	.268	.340	.315	.315	.323
(a)	.090	.265	.380	.248	.165	.205	.185	.185
(b)	.530	.525	.520	.525	.355	.340	.325	.340
(a)	.385	.360	.385	.377	.325	.320	.280	.308
(b)	.390	.375	.345	.370	.325	.290	.275	.297

TABLE 14.—*Coefficients of friction measured at different times on clean wet surfaces with leather soles*

Specimen	Coefficients of friction							
	Measured in 1926				Measured in 1929			
	1	2	3	Average	1	2	3	Average
A (*a*)	0.380	0.360	0.355	0.365	0.590	0.570	0.540	0.
A (*b*)	.770	.770	.770	.770	.730	.730	.710	.
C (*a*)	.270	.220	.195	.228	.405	.390	.370	.
C (*b*)	.490	.485	.485	.487	.740	.750	.740	.
J (*a*)	.270	.315	.270	.285	.270	.325	.350	.
J (*b*)	.560	.610	.625	.598	.570	.615	.615	.
L (*a*)	.560	.560	.590	.570	.510	.490	.485	.
L (*b*)	.740	.720	.780	.737	.625	.650	.675	.
P (*a*)	.750	.640	.610	.667	.750	.760	.750	.
P (*b*)	.820	.790	.770	.793	.780	.730	.770	.
Q (*a*)	.780	.770	.760	.770	.580	.570	.590	.
Q (*b*)	.790	.770	.695	.752	.650	.640	.660	.
V (*a*)	.810	.830	.855	.833	.615	.635	.660	.
V (*b*)	.855	.850	.865	.857	.590	.570	.560	.
W (*a*)	.350	.220	.230	.267	.585	.585	.585	.
W (*b*)	.640	.625	.630	.632	.685	.695	.685	.
X (*a*)	.215	.200	.205	.207	.485	.470	.425	.
X (*b*)	.360	.350	.340	.350	.720	.710	.710	.

IX. DISCUSSION OF FRICTION DATA

In interpreting the preceding data it is important that the relative precision of the different measurements and the reasons for the lack of precision in particular measurements be understood.

The data in Tables 2 and 5 indicate that when constant surfaces are presented the apparatus will duplicate measurements to the nearest 0.005, which is equivalent to an error of ±0.5 per cent for a coefficient of 0.5 or ±2.5 per cent for a coefficient of 0.1. Measurements made on clean, dry surfaces (Table 10) show departures from the original series of measurements ranging for different materials from 0.5 to 9 per cent of the mean of the averages. Measurements on clean, wet surfaces (Table 14) show a wider divergence, ranging for different materials from 0.2 to 38 per cent of the mean.

The measurements on clean, dry surfaces show a reproducibility which would justify the assumption that the coefficient of friction of a material represents approximately its antislip value when the surface is clean and dry. However, it should be noted that some walk-way materials tend to become slippery when the surfaces are dirty or wet or oily and that this tendency bears no relation to the coefficients of friction on clean, dry surfaces. For example, specimen J, a soft, smoothfaced, nonabsorbent material has a higher coefficient when the surface is clean and dry than specimen V, a roughened metal with abrasive embedded in its surface, while measurements on wet and oily surfaces of these same specimens give values in exactly the opposite order. Though these data would enable a rough rating of walk-way materials in respect to their antislip values under each of the simulated service conditions, their direct application to a safety provision for walk-way surfaces seems to be limited, unless the method is further developed and the friction measurements are correlated with the slipping hazard of walk ways in actual service.

The spread in different determinations of the coefficient of friction of the same material, and the possible error in determining the minimum coefficient needed for safety from the meager data available are too great in comparison with the total range in the coefficients of friction of available materials to admit of a strict rating without introducing inconsistencies.

A rough classification of walk-way materials in respect to their safety values under different service conditions could be made from data obtainable by the methods described. This might be accomplished by arranging the materials in the order of their coefficients under each of the simulated service conditions, clean and dry, clean and wet, dirty and wet, and oily. It could be safely assumed that two materials having approximately the same coefficients on clean, dry surfaces will have approximately the same safety values in walk ways with clean, dry surfaces. It could also be safely assumed that two materials showing approximately the same coefficients on clean, wet surfaces will have approximately the same safety values for walk ways with surfaces in that condition, irrespective of what their coefficients are for clean, dry surfaces, and similarly for other simulated or assumed service conditions. Some rule of interpretation embodying these principles is essential before any rational rating of walk-way materials in respect to their safety or antislip values under actual service conditions can be made.

X. SUMMARY OF CONCLUSIONS

1. The apparatus developed for measuring coefficients of friction on walk-way surface materials will duplicate or reproduce its measurement of a given constant coefficient of friction to the nearest 0.005.
2. The coefficient of friction between two materials is a constant only when the condition of the two surfaces remains constant.
3. The coefficient of friction between a shoe sole and a walk-way surface is a variable depending on the smoothness, cleanness, and moisture content of the two surfaces.
4. The precision with which the coefficient of friction between the same sole and the same walk-way material can be reproduced at different times depends on the exactness with which the smoothness, the cleanness, and the dryness can be reproduced, and it varies for different materials.
5. Characteristic differences in frictional properties of walk-way material are shown by their coefficients of friction, measured under dry, wet, and oily conditions, which indicate the tendencies of the materials to become slippery under various service conditions.

WASHINGTON, March 26, 1929.

BEARING BRONZES WITH ADDITIONS OF ZINC, PHOSPHORUS, NICKEL, AND ANTIMONY

By E. M. Staples,[1] R. L. Dowdell,[2] and C. E. Eggenschwiler[3]

ABSTRACT

A study was made of copper-tin-lead-bearing bronzes with and without additions of zinc, phosphorus, nickel, and antimony. Tests made included wear resistance, resistance to impact, Brinell hardness, and resistance to repeated pounding at several temperatures.

In general, the alloys with 4 per cent zinc and the alloys with 0.05 per cent phosphorus gave superior results in the tests as compared with the alloys with nickel and antimony. The alloys with 2 per cent nickel showed decreased wear resistance but increased resistance to pounding, and the alloys with 1 per cent antimony gave low resistance to impact, otherwise these additions were favorable from the standpoint of the other tests.

CONTENTS

	Page
I. Introduction	350
II. Alloys studied	352
III. Preparation of test castings	353
IV. Test methods	354
V. Results and discussion	355
1. Copper-tin-lead bronzes without additions	355
(*a*) Wear resistance	355
(*b*) Resistance to repeated pounding	356
(*c*) Resistance to impact	356
(*d*) Brinell hardness	357
2. Copper-tin-lead bronzes with various additions	357
(*a*) Effect of 4 per cent zinc	357
(1) Structure	357
(2) Wear resistance	358
(3) Resistance to repeated pounding	359
(4) Resistance to impact	359
(5) Brinell hardness	359
(*b*) Effect of 0.05 per cent phosphorus	361
(1) Structure	361
(2) Wear resistance	361
(3) Resistance to repeated pounding	361
(4) Resistance to impact	361
(5) Brinell hardness	361
(*c*) Effect of 2 per cent nickel	361
(1) Structure	362
(2) Wear resistance	362
(3) Resistance to repeated pounding	362
(4) Resistance to impact	362
(5) Brinell hardness	362
(*d*) Effect of 1 per cent antimony	362
(1) Structure	362
(2) Wear resistance	363
(3) Resistance to repeated pounding	363
(4) Resistance to impact	363
(5) Brinell hardness	363
VI. Summary	363
VII. Acknowledgments	364

[1] Research associate, the Bunting Brass & Bronze Co.
[2] Senior Metallurgist, National Bureau of Standards.
[3] Research Assistant, the Bunting Brass & Bronze Co.

I. INTRODUCTION

At the present time there are many specifications for bearing bronzes of the copper-tin-lead type which differ mainly in the amount of other elements contained. The need for most of these specifications may be questioned, when it is considered that the tin and lead contents of these alloys are usually within the range of 0 to 15 per cent and 0 to 30 per cent, respectively. As a large number of bronze alloys having different compositions are used under similar conditions of service, it appears that there is little agreement as to the proper bronze compositions for given service conditions. For example, automotive engineers have diversified opinions as to the most suitable material for wrist-pin bushings. Some specify an alloy with a lead content not to exceed 1 per cent; others indicate that their choice is a material of 10 per cent lead, while still others are of the opinion that wrist-pin bearings should contain from 15 to 20 per cent lead.

In some specifications lead and zinc are classed as impurities, while in others of a similar nature they are listed as essential constituents. Some of the present specifications for bronze-bearing metals are given in Table 1.

In a previous bureau publication [4] the mechanical properties and the testing technique used in determining wear were reported upon for the copper-tin-lead alloys used in railroad equipment. The alloys contained slight amounts of common impurities. In a later bureau publication [5] on bronze bearings the alloys were made from commercially pure materials. It is uneconomical for bearing metals to be made wholly from new or "virgin" metals. The high value of copper, tin, and lead makes the reclamation of unserviceable bearings desirable. These "secondary metals" vary not only in the proportions of copper, tin, and lead, but also in amounts of various other elements, such as zinc, phosphorus, antimony, nickel, iron, etc.

TABLE 1.—*Miscellaneous bearing bronze specifications in present use*

A. BRONZES WITH LOW LEAD CONTENTS

Alloy	Composition (in per cent)															
	Copper		Tin		Lead		Zinc		Phosphorus		Nickel		Antimony, maximum	Iron, maximum	Other elements, maximum
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum			
1	87.0	90.0	9.0	10.0	.....	0.7	0.2	0.5	0.6	0.9	.....	.....	.....	.....	
2	87.7	89.7	9.0	11.0	0.5	1.5	.....	.....	.2	.4	.....	.....	.....	.....	
3	85.7	87.7	9.0	11.0	2.5	3.5	.....	.....	.2	.4	.....	.....	.....	.....	
4	86.0	89.0	9.0	11.0	.....	.2	1.0	3.0	.....	.....	.....	.....	.....	0.06	
5	84.0	85.5	14.5	15.5	.....	.5	.....	.....	.09	.12	.....	.....	.....	.....	
6	85.0	89.0	7.5	8.5	.75	1.5	2.25	4.25	.05	1.0	.....	.....	.....	.....	
7	86.0	88.5	9.0	11.0	1.25	1.6	1.5	2.5	.....	.....	.....	.....	.....	.....	
8	87.0	89.0	9.0	11.0	2.0	3.0	.....	.75	.....	.....	.....	.....	.....	.....	
9	86.0	88.0	9.5	10.5	.6	1.0	1.5	2.5	.....	.....	.....	.....	.....	.....	
10	83.5	85.5	12.5	14.5	.....	.....	1.5	2.5	.....	.....	.....	.....	.....	.....	

[4] H. J. French, S. J. Rosenberg, W. LeC. Harbaugh, and H. C. Cross, Wear and Mechanical Properties of Some Railroad Bearing Bronzes at Different Temperatures, B. S. Jour. Research, 1 (RP13); September, 1928; also Proc. Am. Soc. Test. Matls.; 1928.

[5] H. J. French and E. M. Staples, Bearing Bronzes with and without Zinc, B. S. Jour. Research (RP68); June, 1929; also Proc. Am. Soc. Test. Matls.; 1929.

TABLE 1.—*Miscellaneous bearing bronze specifications in present use*—Continued

A. BRONZES WITH LOW LEAD CONTENTS—Continued

Alloy	Composition (in per cent)														
	Copper		Tin		Lead		Zinc		Phosphorus		Nickel		Antimony, maximum	Iron, maximum	Other elements, maximum
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum			
11	81.0	83.0	9.0	11.0	1.5	3.0	.....	1.0	.....	.....	5.0	7.0	.....	.....	4.5
12	86.7	87.7	8.45	9.95	.....	.....	2.6	3.6	.....	.....	.....	.....	.....	.....	2.25
13	83.0	85.0	11.25	12.75	.....	.5	3.0	4.0	.....	.....	.....	.....	.....	.....	2.75
14	81.0	83.0	9.0	10.5	2.0	3.0	.....	.....	.....	.....	5.0	6.5	.....	.....	3.00
15	86.5	88.5	10.15	11.65	.....	.....	1.1	2.1	.....	.....	.....	.....	.....	.....	2.25
16	89.9	91.9	8.05	9.55	.....	.....	.....	.....	.....	0.30	.....	.....	.....	.....	2.05
17	83.0	85.0	9.25	10.75	2.0	3.0	3.0	4.0	.....	.....	.....	.....	.....	.....	2.75
18	86.0	91.0	6.0	7.0	1.0	2.0	1.5	5.0	.....	.05	.....	.75	0.25	0.15	.20
19	78.0	82.0	4.0	6.0	2.0	3.0	10.0	16.0	.....	.05	.....	.75	.25	.35	.20
20	86.0	89.0	7.5	11.0	.....	.30	1.5	4.5	.....	.05	.....	.75	.25	.25	.40
21	82.0	85.0	13.0	15.0	.....	.20	.....	1.5	.....	.05	.....	.75	.50	.10	.30
22	86.0	89.0	9.0	11.0	1.0	2.50	.....	.....	.....	.25	.....	.....	.....	.....	.50
23	88.0	90.0	10.0	12.0	.....	.....	.....	.....	0.10	.30	.....	.....	.....	.....	.50
24	87.0	89.0	6.5	7.5	1.25	2.75	2.25	3.75	.....	.....	.....	.....	.20	.30	.10
25	87.9	89.0	9.5	10.5	1.0	3.0	.....	.....	.....	.....	.....	.....	.....	.....	.35

B. BRONZES WITH MEDIUM LEAD CONTENTS (4 TO 12 PER CENT)

1	81.0	83.5	6.5	7.5	6.5	7.5	2.5	4.0	.....	0.10	.....	.....	.....	.....	3.5
2	78.5	81.5	9.0	11.0	9.0	11.0	.....	1.0	.....	.....	.....	.....	.....	.....	3.5
3	81.0	87.0	3.0	6.0	4.0	7.5	4.0	6.0	.....	.....	.....	.....	.....	.....	3.0
4	84.0	86.0	4.5	5.5	8.0	10.0	.....	1.50	.....	.....	.....	.....	0.20	0.20	.35
5	83.0	86.0	4.5	6.0	8.0	10.0	.....	2.00	.....	.....	.....	.....	.....	.....	.25
6	78.5	80.5	11.0	13.0	6.5	8.5	.....	1.00	.....	.....	.....	.....	.....	.....	5.00
7	78.5	82.5	9.0	10.5	9.0	10.5	.....	.50	0.60	.90	.....	.....	.....	.....	2.90
8	78.5	81.5	6.5	8.5	10.0	12.0	1.0	2.5	.....	.....	.....	.....	.....	.....	5.00
9	77.0	82.0	9.0	11.0	8.0	11.0	.....	.....	.7	1.0	.....	.....	.....	.....	1.00
10	84.0	86.0	4.0	6.0	4.0	6.0	4.0	6.0	.....	.05	.....	0.75	.25	.25	.20
11	80.0	83.0	2.0	3.0	5.0	7.0	8.0	12.0	.....	.....	.....	.....	.....	.....	1.00
12	82.0	85.0	7.0	9.0	7.0	9.0	.....	.25	.30	.60	.....	1.00	.15	.15	.40
13	83.0	86.0	4.5	5.5	4.5	5.5	4.5	5.5	.....	.....	.....	.....	.25	.35	3.50
14	78.5	81.5	9.0	11.0	9.0	11.0	.....	.75	.05	.25	.....	.....	.....	.....	.25

C. BRONZES WITH HIGH LEAD CONTENTS (12 TO 30 PER CENT)

1	73.0	79.0	6.5	8.0	15.5	18.5	.....	1.00	.....	.....	.....	.....	.....	.....	5.00
2	75.0	79.0	7.0	9.0	13.0	17.0	.....	1.00	.....	.....	.....	.....	.....	.....	5.00
3	68.0	72.0	7.0	9.0	16.0	19.0	.....	1.00	.....	.....	2.50	4.50	.....	.....	5.50
4	73.0	77.0	10.5	11.5	12.0	14.0	0.50	1.50	.....	.....	.....	.....	.....	.....	.50
5	72.0	76.0	4.0	5.0	18.0	22.0	.50	1.0	.....	.....	.....	.....	.....	.....	6.50
6	66.0	77.0	6.0	8.0	23.0	27.0	.....	1.0	.....	.....	.....	.....	.....	.....	4.00
7	71.0	74.5	3.25	4.25	22.0	25.0	.....	.....	.....	.....	.....	.....	.....	.....	3.75
8	69.0	71.0	1.0	2.0	28.0	30.0	.....	.....	.....	.....	.....	.....	.....	.....	2.00
9	73.0	80.0	5.0	7.0	15.0	20.0	.....	.50	.....	0.05	.....	1.00	0.25	0.25	.60
10	75.5	78.5	7.25	8.75	13.50	16.50	.....	.50	.....	.25	.....	.....	.50	.25	.75
11	73.0	.....	9.50	10.50	12.50	15.50	.50	2.50	.....	.....	.....	.25	.20	.20	.20
12	69.0	71.0	4.50	5.50	23.50	26.50	.....	.....	.....	.....	.....	.25	.20	.20	.10
13	69.0	71.0	8.50	9.50	18.50	22.50	.....	.....	.....	.....	.....	.25	.20	.20	.10
14	63.0	72.0	3.0	6.0	23.0	28.0	.....	.....	.....	.....	2.0	3.0	.....	.....	2.00

The subject of impurities is of considerable economic importance in the production of bearing bronzes, the cost of bearings to the consumer being governed largely by the kind and amount of impurities. It is advantageous, therefore, to both the consumer and manufacturer to know the effects of different impurities on the properties. This investigation on the effect of various additions on

the properties of bronzes forms one phase of the general study of bearing bronzes which has been in progress for over two years in cooperation with the Bunting Brass & Bronze Co. on the research associate plan.[6]

II. ALLOYS STUDIED

The program consisted of a study of the effects of various additions, namely, zinc, phosphorus, nickel, and antimony on the properties of copper-tin-lead alloys, most of the alloys studied being selected from the group in common manufacture. In order to widen the scope of the investigation, some alloys, not usually considered as bearing metals, were included.

Five groups of alloys were prepared. In the first group the additions were kept as low as was practicable. In the four additional groups approximately the same ratios of copper-tin-lead were maintained as in the first group, but each group contained an additional metal. These additions consisted of zinc (4 per cent), phosphorus (0.05 per cent), nickel (2 per cent), and antimony (1 per cent). The composition of the various test bronzes are given in Table 2.

TABLE 2.—*Chemical compositions of bronzes studied*

Alloy No.	Used for wear tests (W) or mechanical tests (M)	Chemical composition (in per cent)						
		Copper	Tin	Lead	Zinc	Phosphorus	Nickel	Antimony
10, base alloy	W	96.5	1.8	1.8				
	M	95.4	2.1	2.0				
10Z[1]	W	91.4	2.0	1.9	4.5			
	M	92.5	2.0	1.8	3.7			
10P[2]	WM	96.3	1.6	1.9		0.05		
10N[3]	WM	95.5	.9	1.6			2.0	
10A[4]	WM	95.1	1.8	1.8				1.0
20, base alloy	W	73.7	11.8	14.4				
	M	73.1	12.8	14.1				
20Z	W	69.4	12.1	15.1	3.2			
	M	70.5	11.9	13.8	3.8			
20P	WM	72.9	12.5	14.2		.058		
20N	WM	73.1	12.5	12.3			2.1	
20A	WM	72.7	12.0	13.4				1.3
27, base alloy	W	80.4	10.0	9.5				
	M	79.8	10.3	9.6				
27Z	W	80.5	9.8	9.6				
	W	76.5	9.4	9.8	4.1			
	M	76.4	10.1	9.1	4.4			
27P	W	77.4	9.0	10.1	3.3			
27N	WM	80.7	9.7	9.9		.045		
27A	WM	79.2	9.7	9.1			1.9	
72, base alloy	WM	80.5	9.6	8.6				1.1
72Z	W	85.8	7.3	6.8				
	M	85.3	7.3	7.2				
72P	W	82.2	6.8	7.0	4.0			
72N	M	82.5	7.2	6.7	3.6			
72A	WM	85.7	7.5	6.9		.054		
96, base alloy	WM	84.1	7.1	6.7			2.0	
	WM	84.6	7.2	7.0				1.2
96Z	W	88.1	10.0	2.0				
	W	88.5	9.5	2.0				
	M	88.4	10.3	1.5				
	W	83.9	9.3	2.1	4.4			
	W	84.8	9.9	2.1	3.1			
	M	84.8	9.5	2.0	3.7			

[1] Z, with zinc addition.
[2] P, with phosphorus addition.
[3] N, with nickel addition.
[4] A, with antimony addition.

[6] B. S. Circular No. 296.

TABLE 2.—*Chemical compositions of bronzes studied*—Continued

Alloy No.	Used for wear tests (W) or mechanical tests (M)	Chemical composition (in per cent)						
		Copper	Tin	Lead	Zinc	Phosphorus	Nickel	Antimony
6P	WM	88.4	9.6	2.1		0.043		
6N	WM	87.0	9.0	2.0			1.8	
6A	WM	87.0	9.6	2.3				1.1
25, base alloy	W	75.3	4.5	20.1				
	M	76.6	4.6	18.9				
25Z	W	72.8	4.3	19.1	3.7			
	M	73.0	4.3	18.5	4.2			
25P	WM	75.0	4.8	19.8		.048		
25N	WM	74.9	4.4	18.7			1.9	
25A	WM	78.3	4.3	15.6				1.2
33, base alloy	W	68.2	2.4	28.7				
	M	75.2	1.5	23.2				
33Z	W	66.3	2.2	27.8	3.7			
	M	71.0	1.4	23.8	3.8			
33P	WM	72.5	1.8	25.7		.055		
33N	WM	73.3	1.5	23.1			2.0	
33A	WM	71.1	1.5	25.9				1.1
43, base alloy	W	85.2	14.7					
	M	84.8	15.0					
43Z	W	81.1	14.5		4.4			
	M	82.0	13.8		4.2			
43P	WM	85.0	14.9			.051		
43N	WM	83.4	14.4	.1			1.9	
43A	WM	83.4	15.1	.1				1.1

III. PREPARATION OF THE TEST CASTINGS

In order that the structure and properties of the test castings would approximate those of the average bushings used in the automotive and allied industries, the test castings were of relatively thin section. The dimensions of these test castings, together with the methods of gating, are illustrated in Figure 1.

In the preparation of these castings 1,500 pounds of a base alloy of copper and tin of approximately 90 per cent copper and 10 per cent tin were first melted in an open-flame gas-fired furnace and poured into small notched bar ingots. These ingots were used as the base alloy for subsequent melts; the necessary pure metals being added in order to prepare alloys of desired compositions. These smaller melts, weighing about 40 pounds each, were made in a gas-fired crucible furnace. Additions of zinc, lead, tin, antimony, or phosphorus were added to the molten base alloy after the crucible had been removed from the furnace and carefully skimmed. Additions of copper and nickel were made at the time of charging the crucible. In all cases the metal was melted under a slag of approximately 50 per cent borax and 50 per cent limestone.

All of the heats were poured at temperatures as close as practicable to 2,000° F. (1,095° C.). Deviations from this pouring temperature were slight, with the exception of the alloys Nos. 10 and 133. (Table 2.) The high copper content of alloy No. 10 necessitated a higher pouring temperature, about 2,100° F. (1,150° C.), and on account of the high lead content of alloy No. 133 it was found desirable to pour this alloy at a slightly lower temperature, about 1,950° F. (1,065° C.). Observations made during the process of casting

showed that each of these elements has a strong effect in preventing segregation of lead. It was also noted that melts containing antimony and nickel showed a considerable tendency to oxidize in the crucible and also in the mold.

The casting conditions were kept as nearly constant as possible because it was shown by Carpenter and Elam,[7] Karr,[8] and Rowe[9] that variations in these conditions might appreciably affect the properties of bronzes.

IV. TEST METHODS

In outlining the program special attention was given to the causes of bearing failure in service. Bearings which have failed in service are frequently termed "worn out." This term may often be a misnomer, as wear often plays only a minor part in rendering the bearings unserviceable. Repeated pounding stresses frequently cause a large percentage of failures. A survey of the possible causes of bearing failure indicated that the following properties deserved study: Wear resistance, resistance to repeated pounding, resistance to impact (single-blow), and hardness.

In the work previously reported,[10] wear resistance tests were made both with and without a lubricant, but comparisons of the alloys were made wholly on the basis of the dry or unlubricated tests. "Lubricated tests" would be of value in bearing metal testing technique if such tests were not so difficult to control or did not require such extensive periods of time.

Under conditions of complete film lubrication the wear rate is extremely low. Conditions giving boundary lubrication have many experimental difficulties, so it was decided to run this series of experiments in the unlubricated condition on the Amsler machine.[11]

All wear resistance tests were run in duplicate. Each bronze specimen was tested against a standard steel specimen, a new specimen being used in each case. The steel used throughout this investigation was an oil-hardened carbon steel containing 0.93 per cent carbon. This steel was selected because its surface hardness after treatment is comparable to that of case-hardened low-carbon steel generally used for shafts in bronze bearings. The heat treatment and properties have been previously described.[12]

In the wear-resistance tests the total pressure between the specimens was about 37.5 pounds. The unit contact pressure, as calculated by the Hertz [13] formula, for line contact varied from 24,200 lbs./in.^{2} to 30,600 lbs./in.^{2}, the variation being due to the lateral oscillation of the upper specimen, which is a characteristic feature of the Amsler machine. As these pressures are known to be above the proportional limits of the various bronzes tested, it is believed that the wear rates of the alloys were accelerated accordingly.

---

[7] H. C. H. Carpenter and Miss C. F. Elam, Causes of Unsound Castings of Admiralty Bronze, J. Inst. Met., **19**, p. 155, 1918.
[8] C. P. Karr, Standard Test Specimens of Zinc Bronze, B. S. Tech. Paper No. 59; 1916.
[9] F. W. Rowe, The Effect of Casting Temperature on the Physical Properties of a Sand-Cast Zinc-Bronze, J. Inst. Metals, **31**, p. 217; 1924.
[10] See footnote 5, p. 350.
[11] See footnotes 4 and 5, p. 350.
[12] See footnote 5, p. 350.
[13] Hertz, Miscellaneous Papers, MacMillan & Co. (Ltd.), p. 163; 1896. A more convenient reference is F. H. Buhlman, Factors Governing the Design of Roller Bearings for Roll Necks, Iron & Steel Engr., 4, p. 302; June 1927.

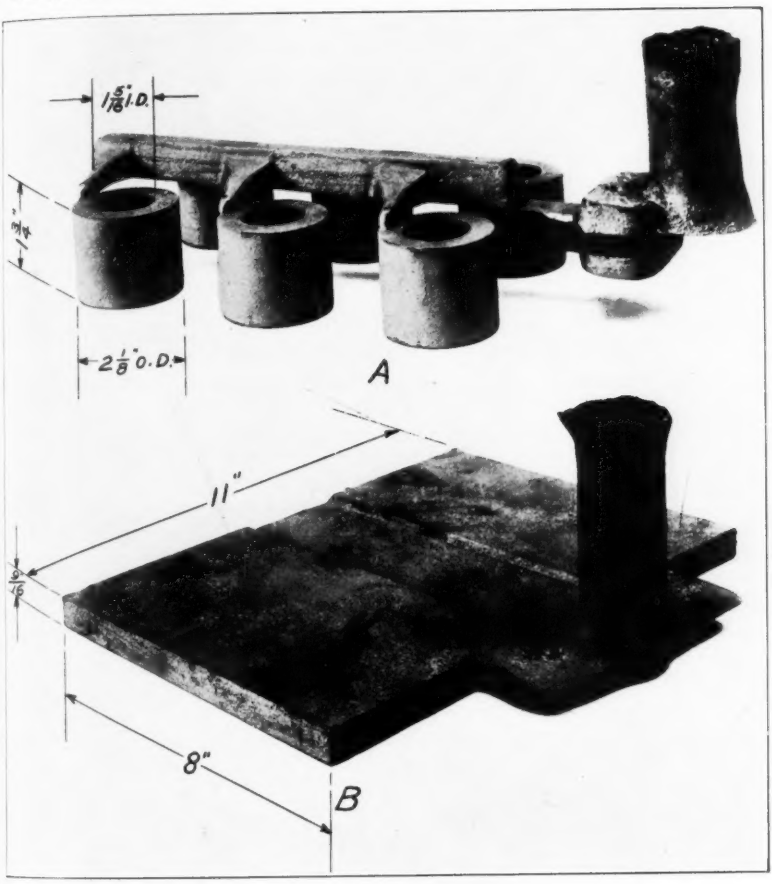


FIGURE 1.—*Test castings*

A, For wear test specimens; *B*, for impact, pounding and hardness tests.

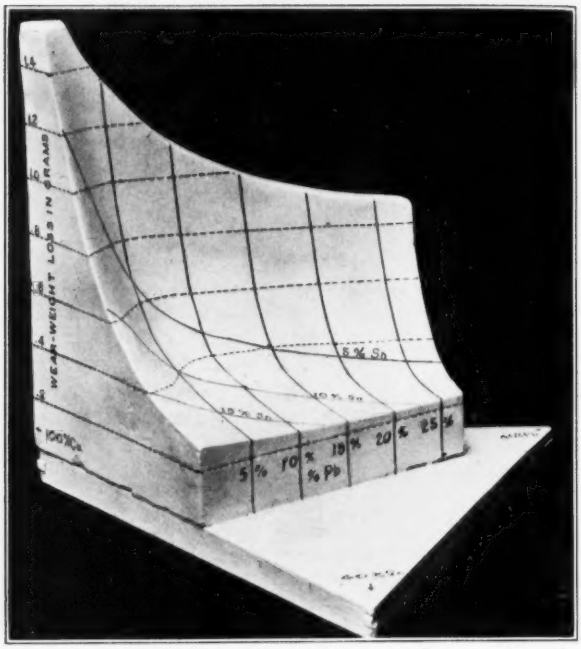


FIGURE 3.—*Model showing relation for bronzes investigated in Cu-Sn-Pb system*

Wear expressed in weight loss per 10,000 revolutions. Test conditions are described in detail in the reference given in footnote 1 of the text. Tests made at atmospheric temperatures.

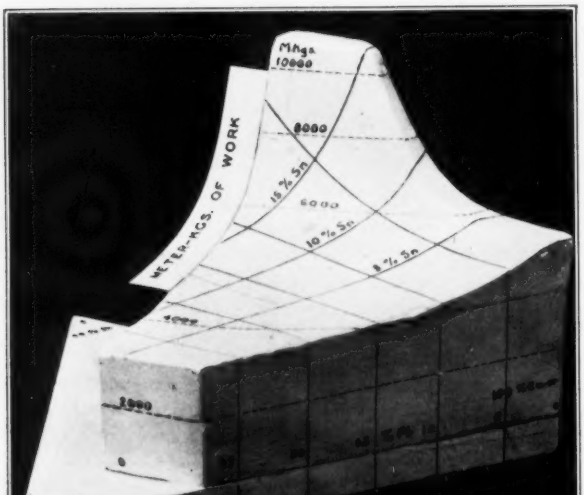


FIGURE 4.—*Model showing relation of work done in meter-kilograms per 10,000 revolutions for bronzes investigated in the Cu-Sn-Pb system*

The meter-kilogram of work is determined from the torque indicator of the Amsler wear machine, and is directly proportional to the frictional force between the steel and the bronze specimens. Tests made at atmospheric temperatures.

The equipment and methods of test used for the determination of resistance to pounding, resistance to impact, and Brinell hardness have been previously described.[14]

The forms of test specimens used for the determination of wear, resistance to impact, and resistance to repeated pounding are shown in Figure 2.

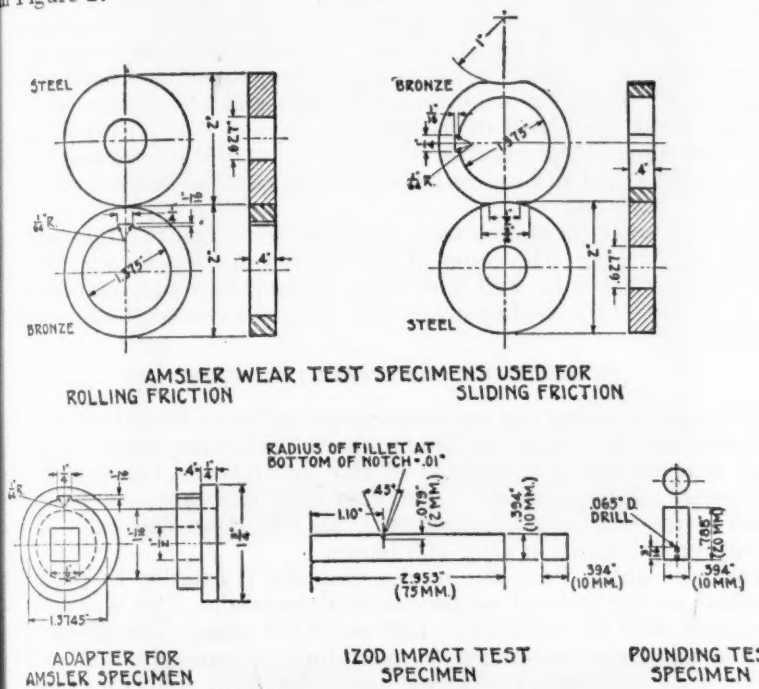


FIGURE 2.—*Forms of test specimens*

V. RESULTS AND DISCUSSION

1. COPPER-TIN-LEAD BRONZES WITHOUT ADDITIONS

(a) WEAR RESISTANCE

The results of tests on wear resistance of the alloys without additions are shown by the ternary model (fig. 3), in which the ordinates show weight losses for 10,000 revolutions obtained with the different alloys represented in the base of the model. It will be noted that an increase in the content of tin and lead, either collectively or separately, reduced the rate of wear. Other information of value was obtained from these tests, particularly the frictional force between the bronze and the steel as measured by the torque indicator. Some of the specimens tested for wear resistance showed a tendency to "flat-wheel" or become "out of round" during testing. Alloys having high resistance to pounding do not "flat-wheel" during the test, while alloys having low resistance to pounding show the greatest tendency toward the "flat-wheel" effect.

[14] See footnote 5, p. 350.

The average results indicative of the relative friction between th bronzes and the steel specimens during testing are given in the terna model, as meter-kilograms of work recorded by the torque indicat (Fig. 4.) Attention is called to the fact that the coefficient of frict of a bearing material with a journal, tested under unlubricat conditions, has no apparent relationship to the coefficient of frict of the same bearing and shaft if adequate lubrication is maintain When lubrication is incomplete, such as during starting or failure the lubricant, the coefficient of friction of the journal and bearing is importance. In order to minimize damage and seizure due to ov heating, a low coefficient of friction is desirable. Attention is call to the increase in the number of kilograms of work recorded by t torque indicator with bronzes having a lead content below 5 per ce (Fig. 4.)

Tests on wear resistance were made at room temperature and 350° F. (175° C.). The order of comparison of the alloys at 350° (175° C.) agreed quite well with that obtained at room temperatur but a consistently higher wear rate was observed at the high temperature.

(b) RESISTANCE TO REPEATED POUNDING

The model showing the resistance to pounding of the alloys witho additions (fig. 5) is based on the number of blows required to produ 5 per cent deformation (upset) of the specimens. As some of t specimens did not deform 5 per cent, the resistance to poundi of the series with the additions was measured on the basis of t percentage deformation after 100 blows.

It will be noted from the model that the resistance to poundi increased as the ratio of copper to tin decreased. This was inves gated only with tin contents as high as 15 per cent. The effect of t on increasing the resistance to pounding is probably due to tw causes; first, a strengthening of the alpha solid solution of tin copper, and second, a further stiffening of the resulting structure b the precipitation of the delta microconstituent according to t reaction beta → alpha plus delta.

It would seem that additions of lead would lower considerably t pounding resistance, but it should be remembered that the ratio copper to tin is of prime importance, because it is largely the matrix the alloy that resists deformation and not the free lead contained.

(c) RESISTANCE TO IMPACT

Impact tests by the Izod method were made on all of the allo studied. The value of this test for comparing bearing metals largely dependent on the design of the bearing. Bearings complete supported need not necessarily be of high toughness. On the oth hand, if the bearing has overhanging flanges or unsupported par which might be subjected to shock, the relative toughness of t bearing metal is of importance.

The notch toughness values obtained on the alloys without add tions are shown in a ternary model. (Fig. 6.) It was found th an increase in tin, to about 8 per cent, had little effect. When t tin content was above that amount, a sharp decrease in toughne resulted, due primarily to the brittleness of the alpha-delta micr

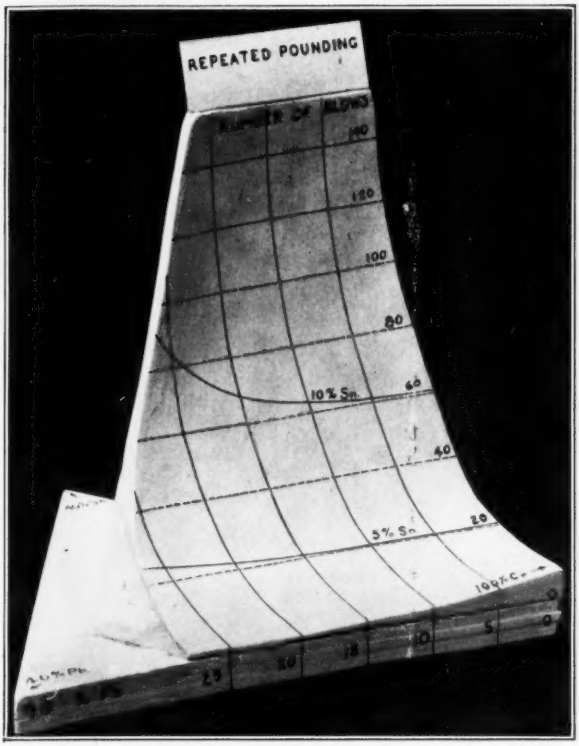


FIGURE 5.—*Model showing relation of repeated pounding for bronzes investigated in the Cu-Sn-Pb system*

Test is one of "upsetting" where comparisons are based on the number of blows producing 5 per cent deformation. Tests made at atmospheric temperatures.

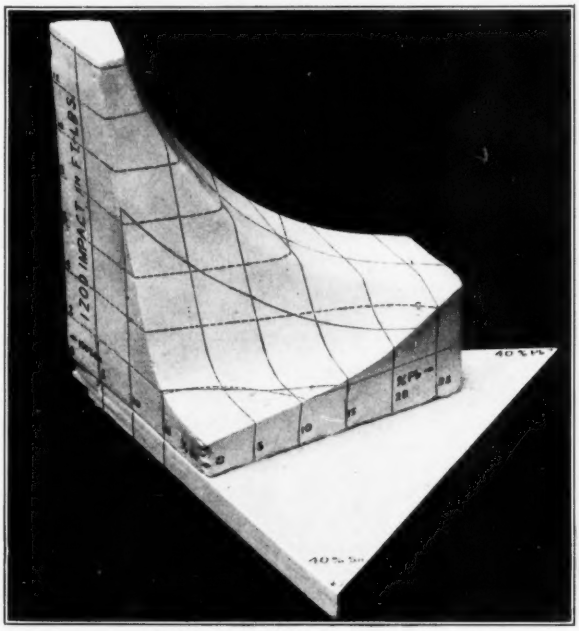


FIGURE 6.—*Model showing relation of izod impact resistance for bronzes investigated in the Cu-Sn-Pb system*

Tests made at atmospheric temperatures

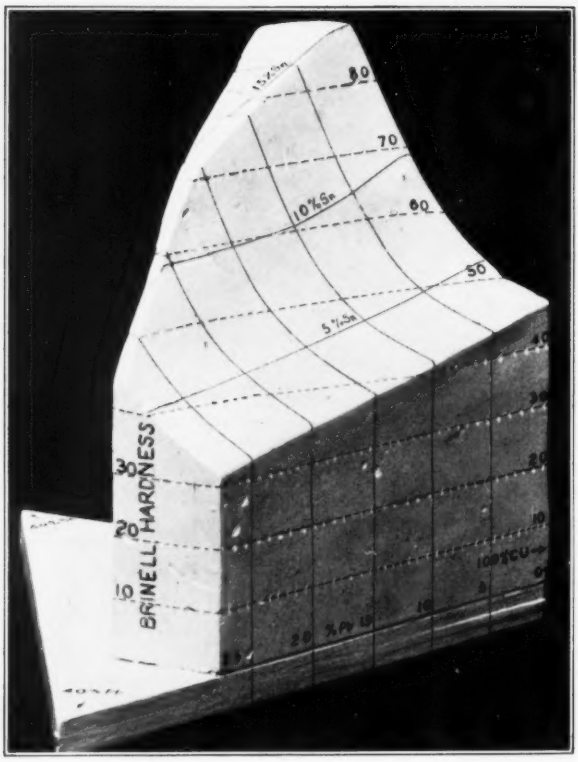


FIGURE 7.—*Model showing relation of Brinell hardness for bronzes investigated in Cu-Sn-Pb system*

Tests with 500 kg. load and 10 mm. ball at atmospheric temperatures.

nstituent.[15] A progressive increase in the lead content produced gradual decrease in toughness. Evidently this was because free ad is relatively very low in its impact toughness and also because e occurrence of the particles of lead in the bronze matrix reduced e effective cross section of the specimen.

(d) BRINELL HARDNESS

The results of Brinell hardness tests (10 mm ball and 500 kg load) the alloys without additions are shown in Figure 7. The Brinell rdness reported on the alloys without additions showed the exected trends—that is, an increase in hardness with an increase in e tin content and a gradual decrease with a progressive increase the lead content. Attention is called to the fact that no definite lationship has, as yet, been found between hardness and resistance pounding. Alloys of the same hardness may differ in resistance pounding, while, on the other hand, alloys of different hardnesses ay have the same resistance to pounding.

2. COPPER-TIN-LEAD BRONZES WITH VARIOUS ADDITIONS

A comparison of the various properties determined on the copper-n-lead bronzes with and without additions of 4 per cent zinc, 0.05 r cent phosphorus, 2 per cent nickel, and 1 per cent antimony is ven in Figures 8, 9, 10, and 11.

(a) EFFECT OF 4 PER CENT ZINC

Zinc is frequently added to copper-tin alloys as a deoxidizer to prove their soundness. The constitution and mechanical proper-s of these alloys, known as copper-rich kalchoids, have been de-mined by a number of investigators, Hoyt,[16] Guillet,[17] Guillet and villon,[18] Thurston,[19] Miller.[20] Portevin and Nusbaumer [21] reported sults from a Derihon machine and found that bronze alloys con-ning about 2.5 per cent zinc with 5 to 10 per cent tin had higher ar resistance than alloys without zinc, but having high tin con-nts (13 to 19 per cent).

(1) *Structure.*—The micrographs given in this report show the fects on the structure of the additions investigated, namely, 4 per nt zinc, 0.05 per cent phosphorus, 2 per cent nickel, and 1 per nt antimony, on a copper-tin-lead alloy which was basically 80 r cent copper, 10 per cent tin, and 10 per cent lead. Figures 12, , 14, 15, and 16 show the structures of these alloys with and with-t the additions in the unetched and etched conditions.

The addition of 4 per cent zinc to the base alloy produced no ange in either the distribution or the segregation of lead. (Figs. (*a*) and (*b*).) A comparison of Figures 12 (*b*) and 13 (*b*) shows at the addition of 4 per cent zinc increased the relative amount

---

W. L. Kent, The Brittle Ranges of Bronze, J. Inst. of Metals (British), **35**, pp. 45–51; 1926.
S. L. Hoyt, On the Copper-Rich Kalchoids, J. Inst. Metals, **10**, p. 235; 1913.
L. Guillet, Étude Générale des Tritons Spéciaux, Rev. de Met., Memoirs, **3**, p. 243; 1906.
Guillet and Revillon, Determinations of the Coefficient of Equivalence for Special Bronzes, Rev. Mem., **7**, p. 429; 1910.
R. H. Thurston, Materials of Engineering, Pt. III. Brasses, Bronzes, John Wiley & Sons (4th ed.), p. 100.
Von Honnes v. Miller, Studien über die Einwirkung der Wichtigeren metallischer und nicht-allischen Zusätze auf normale Kupfer-Zinn Bronze, Metallurgie, **9**, p. 63; 1912.
Portevin and Nusbaumer, Essais sur l'Usure des Bronzes, Rev. de Metallurgie, **9**, p. 61; 1912.

of the eutectoid constituent (alpha and delta) over that of the alloy without additions. The increased amount of the eutectoid constituent in the zinc alloys probably accounts for the fact that the "wearing-in" period of the specimens in the Amsler test was greater than in the case of the base alloy of only copper, tin, and lead.

(2) *Wear resistance.*—In a previous paper [22] the effects produced on a number of bearing bronzes by the addition of 4 per cent zinc

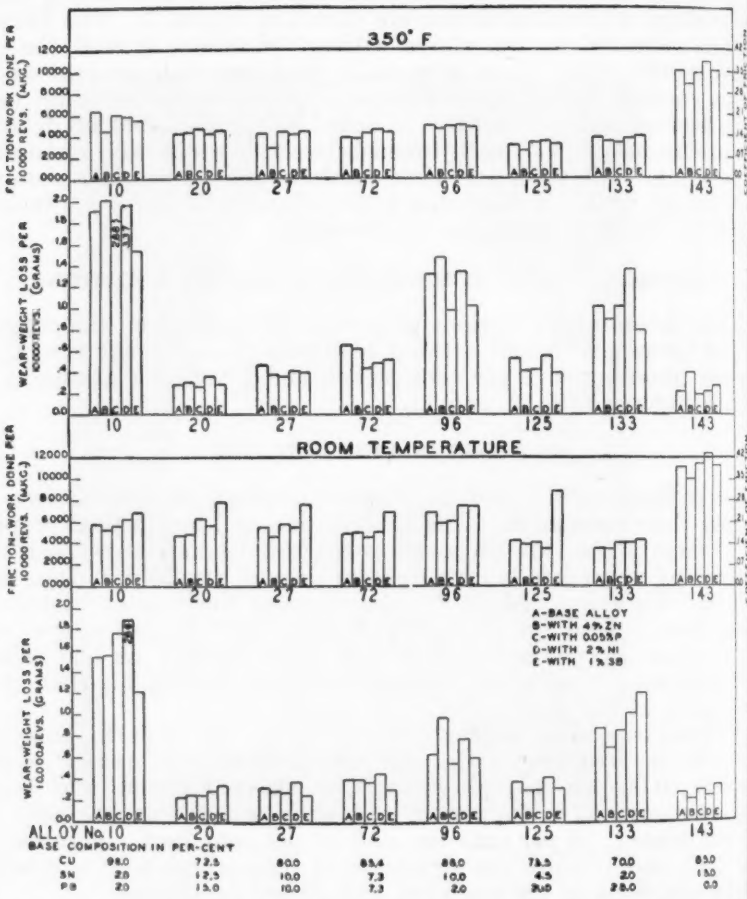

350° F
ROOM TEMPERATURE
FRICTION-WORK DONE PER 10000 REVS. (MKG.)
WEAR-WEIGHT LOSS PER 10000 REVS. (GRAMS)
A-BASE ALLOY
B-WITH 4% ZN
C-WITH 0.05% P
D-WITH 2% NI
E-WITH 1% SB
ALLOY No. 10 20 27 72 96 125 133 143
BASE COMPOSITION IN PER-CENT
CU 98.0 72.5 80.0 83.4 88.0 72.5 70.0 83.0
SN 2.0 12.5 10.0 7.3 10.0 4.5 2.0 15.0
PB 2.0 15.0 10.0 7.3 2.0 23.0 28.0 0.0

FIGURE 8.—*Comparison of wear characteristics of Cu-Sn-Pb bronzes with and without other additions*

Tests made at room temperatures and at 350° F. (175° C.).

have been discussed in detail. In the present investigation the rate of wear of alloy containing 4 per cent zinc at room temperature was about the same as that of the alloys containing no added impurities with the exception of alloy No. 96. In this alloy, basically 88 per cent copper, 10 per cent tin, and 2 per cent lead, the addition of 4 per cent zinc caused an increase of about 53 per cent in the wear

[22] See footnote 5, p. 350.

rate at room temperature but only 12 per cent at 350° F. (175° C.). With the exception of alloy No. 96, and perhaps No. 133, it may be said that the addition of 4 per cent zinc does not have an appreciable effect on the wear resistance or the frictional forces between the copper-tin-lead alloys and steels.

(3) *Resistance to repeated pounding.*—The addition of 4 per cent zinc increased the resistance to pounding of the alloys at room temperature, but had little effect at temperatures of 350° F. (175° C.). At 600° F. (315° C.), however, the tendency was toward decreased resistance to pounding. Some of the alloys containing zinc showed less deformation at the end of 100 blows than the companion alloys

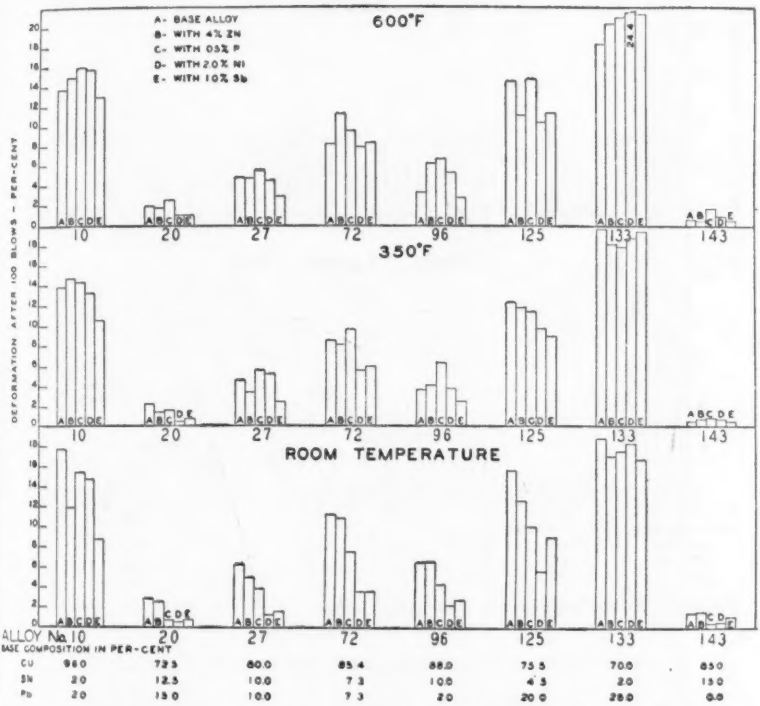

A- BASE ALLOY
B- WITH 4% ZN
C- WITH 03% P
D- WITH 20% NI
E- WITH 10% Sb
600°F
350°F
ROOM TEMPERATURE
DEFORMATION AFTER 100 BLOWS - PER-CENT
ALLOY No. 10 20 27 72 96 125 133 143
BASE COMPOSITION IN PER-CENT
Cu 80 72.5 80.0 85.4 88.0 73.5 70.0 85.0
Sn 20 12.5 10.0 7.3 10.0 4.5 2.0 13.0
Pb 20 15.0 10.0 7.3 2.0 20.0 28.0 0.0

FIGURE 9.—*Comparison of the resistance to repeated pounding of Cu-Sn-Pb bronzes with and without other additions*

Tests made at room temperature, 350° F. (175° C.) and 600° F. (315° C.).

containing no zinc. In other cases greater deformation was obtained with the alloys containing zinc. The differences, however, were slight, and for practical purposes it may be stated that the addition of 4 per cent zinc has little effect on the resistance to deformation.

(4) *Resistance to impact.*—The addition of 4 per cent of zinc had a tendency to increase the resistance to impact of the alloys studied at both room temperature and elevated temperatures.

(5) *Brinell hardness.*—Of the alloys studied, those with zinc were consistently harder than those without zinc. The increase in hardness attributable to the addition of 4 per cent zinc was slight, however.

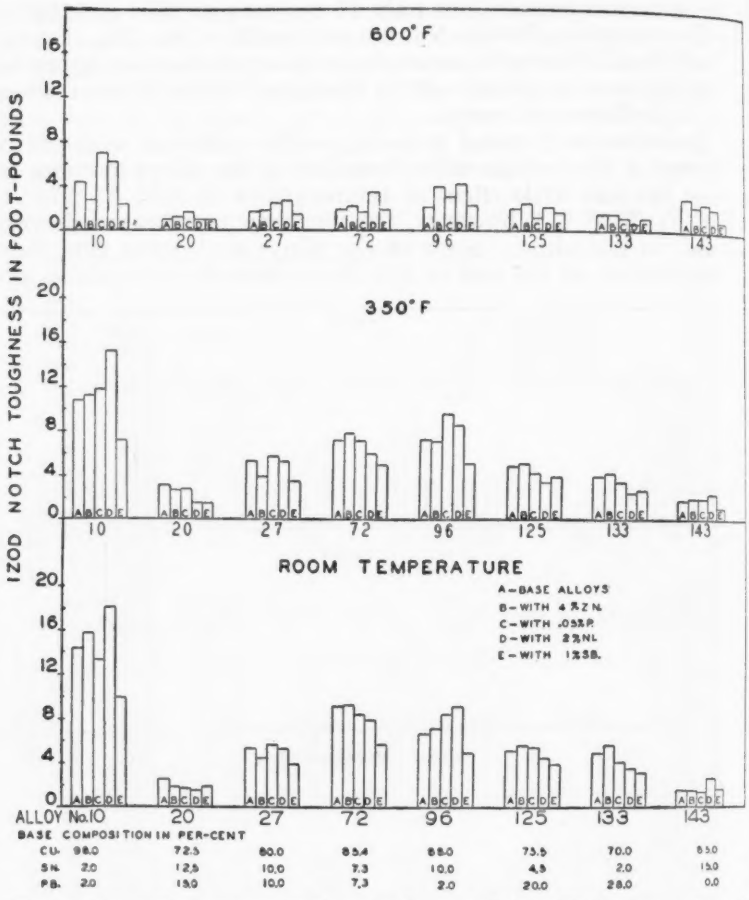

600° F
350° F
ROOM TEMPERATURE
IZOD NOTCH TOUGHNESS IN FOOT-POUNDS
A-BASE ALLOYS
B-WITH 4 %ZN.
C-WITH .05%P.
D-WITH 2%NI.
E-WITH 1%SB.
ALLOY No. 10 20 27 72 96 125 133 143
BASE COMPOSITION IN PER-CENT
CU 98.0 72.5 80.0 85.4 88.0 73.5 70.0 85.0
SN 2.0 12.5 10.0 7.3 10.0 4.5 2.0 13.0
PB. 2.0 15.0 10.0 7.3 2.0 20.0 28.0 0.0

FIGURE 10.—*Comparison of impact values of Cu-Sn-Pb bronzes with and without other additions*

Tests made at room temperatures, 350° F. (175° C.) and 600° F. (315° C.).

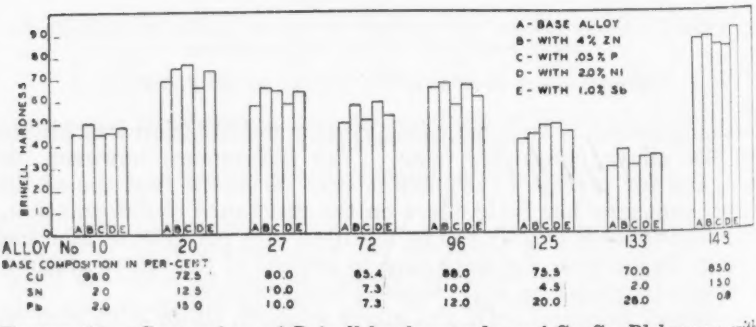


FIGURE 11.—*Comparison of Brinell hardness values of Cu-Sn-Pb bronzes with and without other additions*

All tests made at room temperatures.

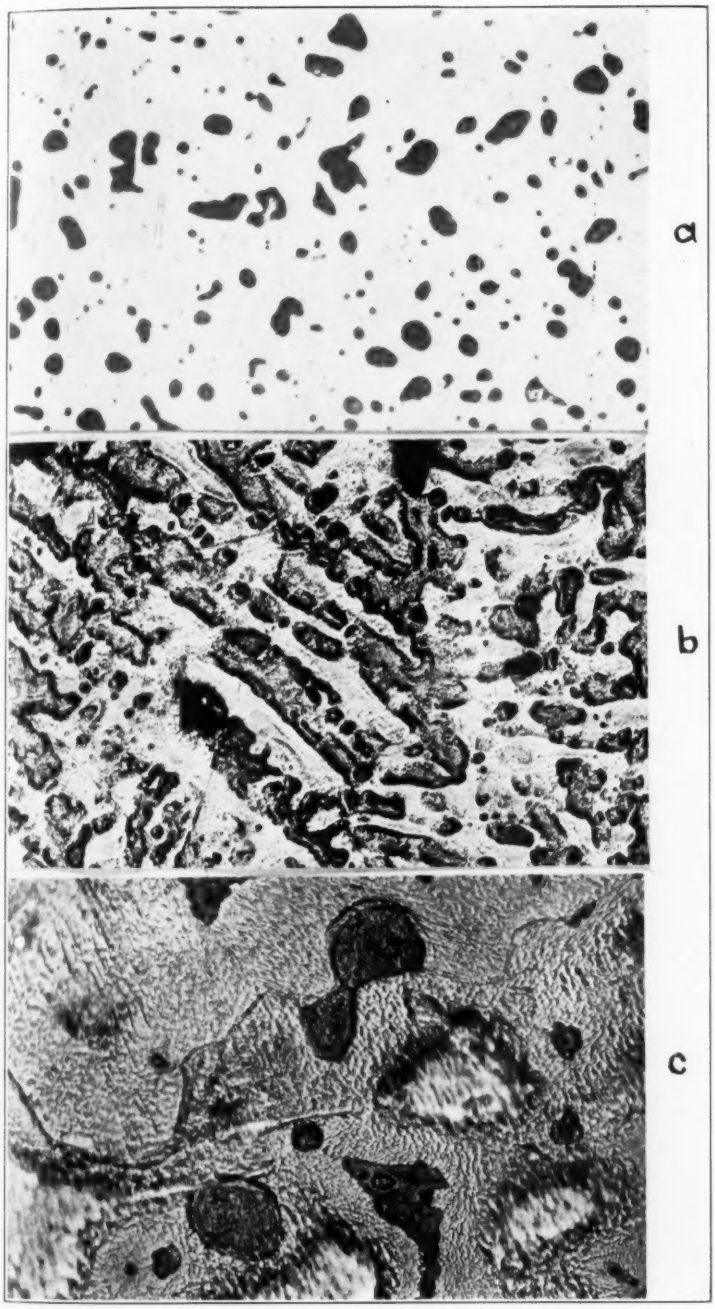


FIGURE 12.—*Microstructure of 80-10-10 bronze without additions*

a, Unetched, × 100; *b*, etched, × 100; *c*, etched, × 500. Etchant 3 parts NH_4OH plus 1 part H_2O_2, followed by solution of $FeCl_3$ in HCl (10 g $FeCl_3$ plus 30 ml HCl plus 120 ml H_2O).

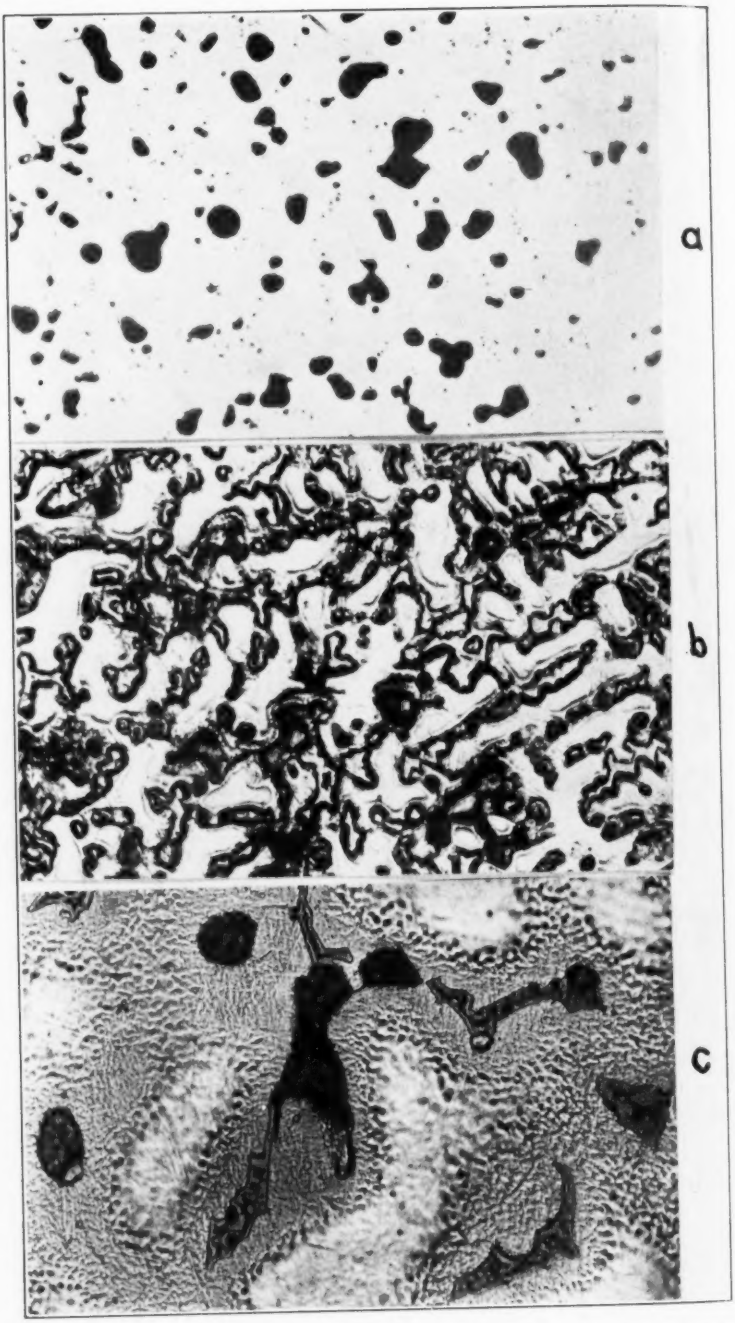


FIGURE 13.—*Microstructure of 80-10-10 bronze with addition of 4 per cent zinc*

Unetched, × 100; *b*, etched, × 100; *c*, etched, ×500. Etchant 3 parts NH_4OH plus 1 part H_2O_2, followed by solution of $FeCl_3$ in HCl (10 g $FeCl_3$ plus 30 ml HCl plus 120 ml H_2O).

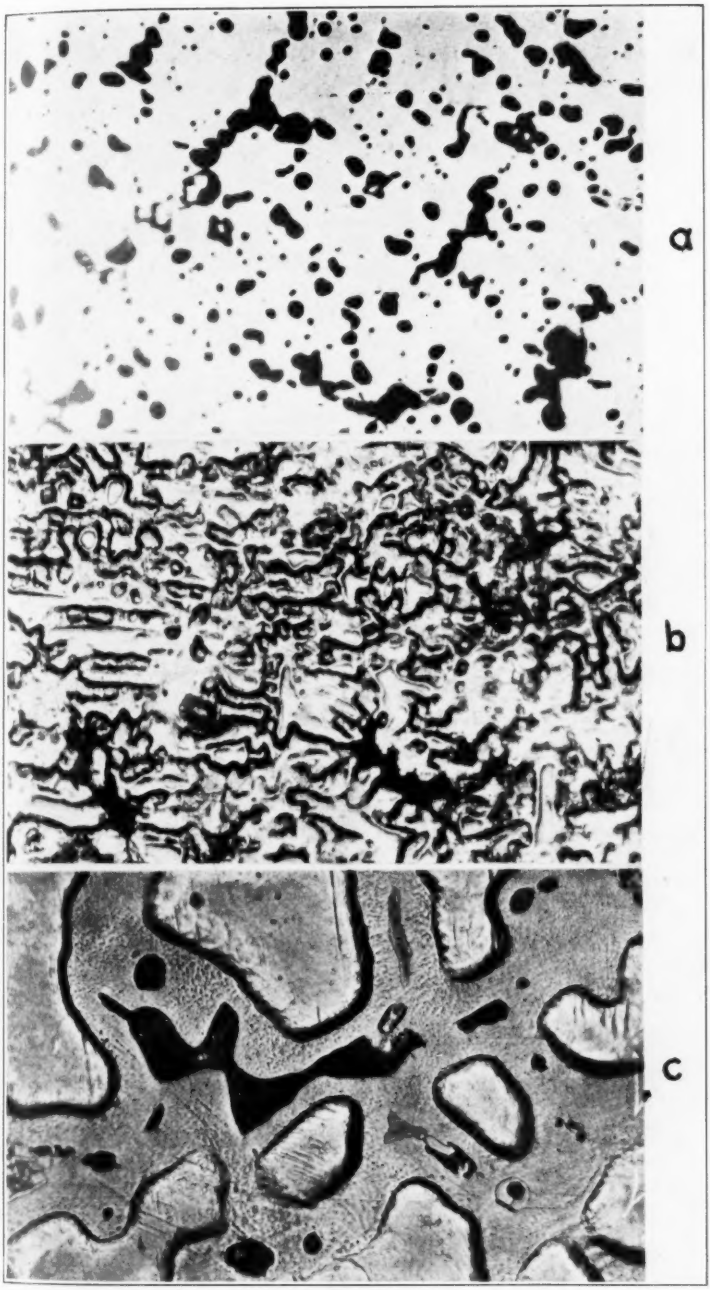


FIGURE 14.—*Microstructure of 80-10-10 bronze with addition of 0.05 per cent phosphorus*

a, Unetched, × 100; *b*, etched, × 100; *c*, etched, × 500. Etchant 3 parts NH_4OH plus 1 part H_2O_2, followed by solution of $FeCl_3$ in HCl (10 g $FeCl_3$ plus 30 ml. HCl plus 120 ml H_2O).

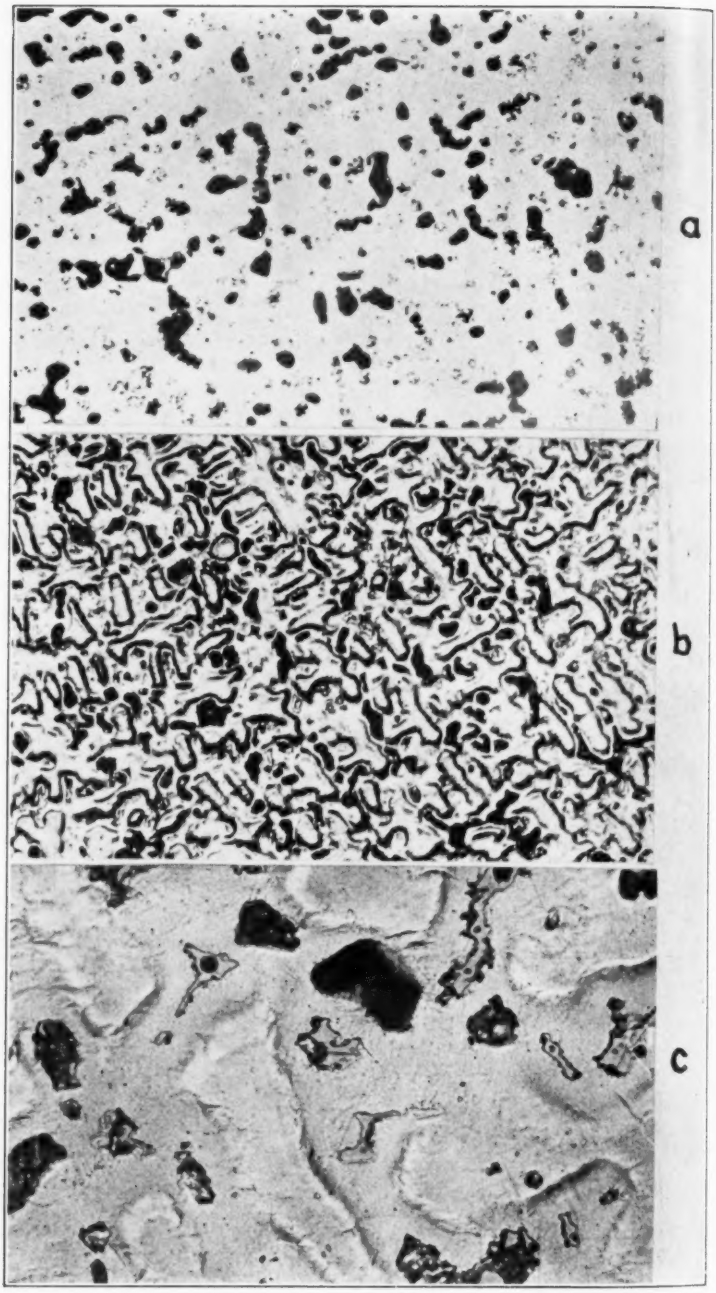


FIGURE 15.—*Microstructure of 80-10-10 bronze with addition of 2 per cent nickel*

a, Unetched, × 100; *b*, etched, × 100; *c*, etched, × 500. Etchant 3 parts NH_4OH plus 1 part H_2O_2, followed by solution of $FeCl_3$ in HCl (10 g $FeCl_3$ plus 30 ml HCl plus 120 ml H_2O).

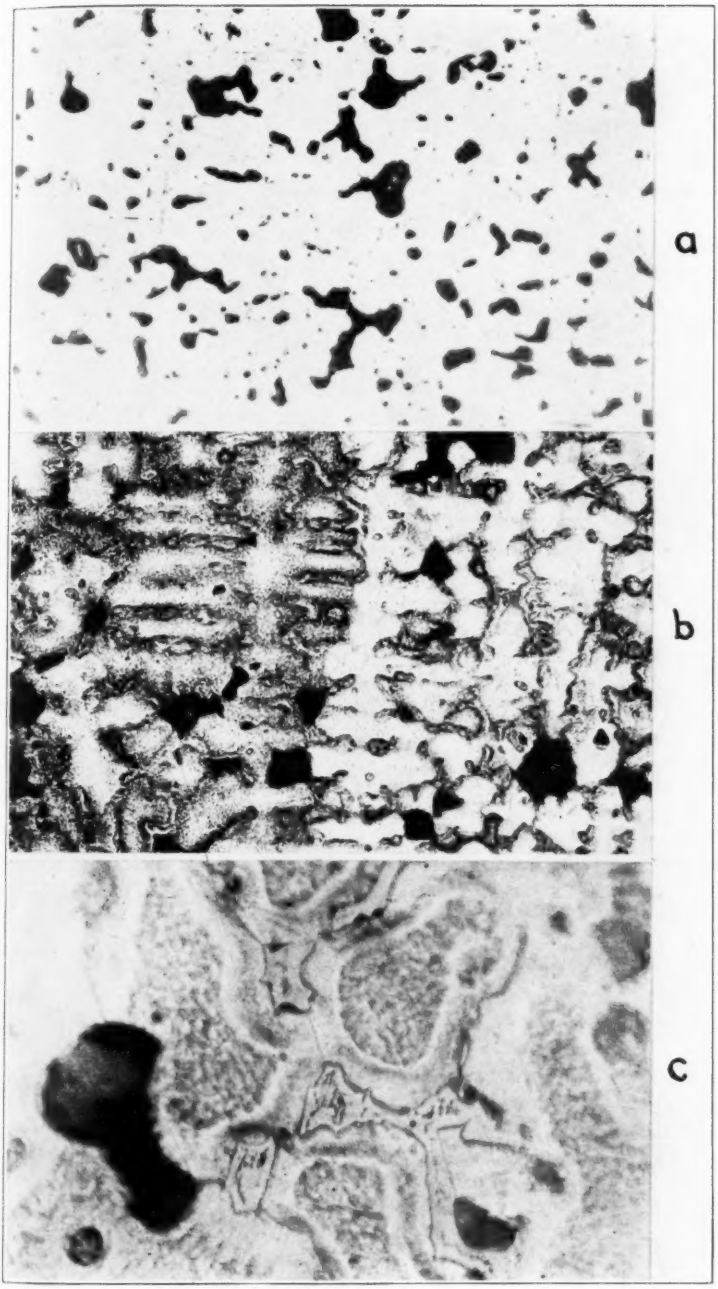


FIGURE 16.—*Microstructure of 80-10-10 bronze with addition of 1 per cent antimony*

a, Unetched, × 100; *b*, etched, × 100; *c*, etched, × 500. Etchant 3 parts NH_4OH plus 1 part H_2O_2, followed by solution of $FeCl_3$ in HCl (10 g $FeCl_3$ plus 30 ml HCl plus 120 ml H_2O).

In some respects the results previously reported confirm those of Clamer,[23] who found that the addition of zinc to leaded bronzes hardened the alloys and increased the wear rate, but he concluded that the alloys having approximately 5 per cent tin, up to 20 per cent lead, and up to 5 per cent zinc should be entirely satisfactory for all classes of car-journal bearings.

(b) EFFECT OF 0.05 PER CENT PHOSPHORUS

Phosphorus is frequently added to deoxidize bronze and is generally added as phosphor-copper, although stick phosphorus is sometimes used. Phosphor bronze occasionally contains as much as 1 per cent phosphorus. Bronzes containing about 0.7 per cent phosphorus have been reported to have desirable mechanical properties by Philip [24] and others.

(1) *Structure.*—The addition of 0.05 per cent phosphorus to the base alloy of 80 per cent copper, 10 per cent tin, and 10 per cent lead appears to minimize the segregation of lead. (Figs. 12 (*a*) and 14 (*a*).) The grain size of the alloys containing phosphorus is finer than with the alloys without 0.05 per cent phosphorus. (Figs. 12 (*b*) and 14 (*b*).) This finer grain size may be largely responsible for the increased Brinell hardness and increased resistance to wear which was found for these alloys.

(2) *Wear resistance.*—In general, the addition of 0.05 per cent phosphorus was found to increase slightly the wear resistance, but not appreciably to affect the frictional force. Most of the alloys containing phosphorus showed a higher wear resistance than the base alloy at room temperature and at 350° F. (175° C.). However, alloy No. 10, basically 96 per cent copper, 2 per cent tin, and 2 per cent lead, showed the addition of phosphorus to be deleterious at both temperatures.

(3) *Repeated pounding.*—All of the alloys tested showed a consistent and appreciable effect of phosphorus on the resistance to pounding. At room temperature this effect was to increase the resistance to deformation, while at 350° F. (175° C.) there was little effect and at 600° F. (315° C.) there was a reduction in the resistance to deformation.

(4) *Resistance to impact.*—The addition of 0.05 per cent phosphorus had no marked effect on the notch toughness at either room temperature or 350° F. (175° C.). At 600° F. (315° C.) there was a tendency toward a slight increase in toughness.

(5) *Brinell hardness.*—Of the 8 alloys, with and without phosphorus, which were tested, 6 showed a slightly increased hardness due to the phosphorus addition, while for 2 the opposite was true. The magnitude of the effects found was not great, so it may be said that the phosphorus addition has little effect on the Brinell hardness, although the tendency seems to be toward an increase in hardness.

(c) EFFECT OF 2 PER CENT NICKEL

The results from the tests with bronzes which contained nickel were somewhat analagous with those of Corse,[25] who has reported that the tensile strength and elongation of 80–10–10 bronze is improved by the

[23] G. H. Clamer, Effect of Changes in the Composition of Alloys Used by the American Railways for Car Journal Bearings, Trans. Am. Inst. Metals, **9**, p. 241; 1915.
[24] A. Philip, J. Inst. Metals, **1**, No. 1, p. 174; 1909.
[25] W. M. Corse, Nickel in Brass and White Metals, Met. Ind. (N. Y.), **22**, p. 234; 1924.

addition of 1 per cent nickel. He has also stated that nickel additions also increase the rate of cooling and thereby reduce to a minimum the tendency toward lead segregation.

(1) *Structure.*—The alloys containing nickel (2 per cent) showed a finer distribution, less segregation of the lead, and also a finer-grain size than the comparison alloys containing no nickel. (Figs. 12 (*a*) and (*b*) and 15 (*a*) and (*b*).) It should be noted that the eutectoid constituent of the nickel alloy was comparatively free from alpha (fig. 15 (*c*)) and occurred frequently in direct contact with lead particles. This may account in part for the higher frictional forces and the decrease in wear resistance.

(2) *Wear resistance.*—All alloys containing 2 per cent nickel with the exception of No. 143, having a base composition of 85 per cent copper and 15 per cent tin, showed increased wear rates at room temperature. At 350° F. (175° C.) alloys Nos. 27 and 96 containing 80 copper, 10 tin, and 10 lead, and 88 copper, 10 tin, and 2 lead, respectively, gave results indicating a slightly beneficial effect of nickel. In general, the addition of 2 per cent nickel increased the wear rate of the alloys and slightly increased the frictional force as measured by the torque indicator.

(3) *Repeated pounding.*—A noteworthy advantage gained by the addition of 2 per cent nickel is apparent from the results of the pounding tests at room temperature. With the exception of those alloys very low in tin, Nos. 10 and 133, the addition of 2 per cent nickel increased the resistance to deformation of the alloys about 300 per cent. At 350° F. (175° C.) the beneficial effect of nickel was not as apparent as at room temperature, while at 600° F. (315° C.) there was no beneficial effect.

(4) *Resistance to impact.*—In the alloys containing low amounts of lead, Nos. 10, 96, and 143, the addition of 2 per cent nickel increased the resistance to impact at the three test temperatures; however, there was a decrease with alloy No. 143 at the test temperature of 600° F. (315° C.). However, with alloys containing over 2 per cent lead, there was, in general, a slight decrease in toughness.

(5) *Brinell hardness.*—The addition of 2 per cent nickel produced no marked effect on the hardness of the alloys studied, although there appeared to be a slight tendency toward an increase in hardness.

(d) EFFECT OF 1 PER CENT ANTIMONY

Antimony is nearly always considered an undesirable impurity in bronze. It has been stated, however, by Rolfe [26] that antimony frequently occurs in gun metal, sometimes so high as 1 per cent, and that gun-metal castings containing from 0.5 to 1 per cent antimony do not show any marked falling off in the mechanical properties. In a later publication, however, the same author [27] has stated that the effect of higher amounts of antimony is to increase progressively the hardness and brittleness and cause a progressive falling away in the strength and ductility. No difference in soundness or microstructure was reported.

(1) *Structure.*—In the alloys studied the addition of 1 per cent antimony to the base alloy of 80 per cent copper, 10 per cent tin, and

[26] R. T. Rolfe, Note on the Effect of Arsenic, Antimony, and Lead on 88–10–2 Gun Metal, J. Inst. Met., **20**, p. 263; 1918.

[27] R. T. Rolfe, The Effect of Increasing Proportions of Antimony and Arsenic, Respectively, upon the Properties of Admiralty Gun Metal, J. Inst. Met., **24**, p. 233; 1920.

10 per cent lead appeared to increase the segregation of lead. (Figs. 12 (*a*) and 16 (*a*).) The addition of antimony did not appear to affect the general grain size of the alloy. It is probable that the antimony is largely alloyed with the lead and results in a lower wear resistance as compared with the base alloy without antimony. (Figs. 12 (*b*) and (*c*) and 16 (*b*) and (*c*).)

(2) *Wear resistance.*—Although the addition of 1 per cent antimony in most instances increased the wear resistance of the alloys studied, it also increased the friction. At room temperature, the indicated friction of the alloys containing antimony was considerably higher than of those without antimony. This effect was not so noticeable at 350° F. (175°C.) as at room temperature.

(3) *Resistance to repeated pounding.*—There was a beneficial effect produced by 1 per cent antimony as regards the resistance to pounding. Increases as high as 300 per cent were noted at room temperature, while at 350° F. (175° C.) and 600° F. (315° C.) the advantage gained by adding antimony was still apparent.

(4) *Resistance to impact.*—Probably the most definite effect of antimony was to decrease the resistance to impact of copper-tin-lead alloys. In most of the alloys studied at the three test temperatures the addition of 1 per cent antimony reduced the resistance to impact about 30 per cent.

(5) *Brinell hardness.*—The addition of 1 per cent antimony had little effect on the hardness of the alloys studied, although there seemed to be a tendency toward an increase.

VI. SUMMARY

Copper-tin-lead-bearing bronzes, high in copper, have been studied by the application of various mechanical tests, such as Brinell hardness, resistance to impact, resistance to repeated pounding, and resistance to wear.

The effects of several additions, 4 per cent zinc, 0.05 per cent phosphorus, 2 per cent nickel and 1 per cent antimony have been studied by the application of the individual tests previously mentioned.

The results of the study of the effects of different additions on the properties of bearing bronzes are briefly summarized in Table 3.

TABLE 3.—*General effects of additions studied on properties of bronzes*

Addition	Property			
	Wear resistance (Amsler test)	Resistance to pounding	Resistance to impact (Izod)	Brinell hardness
per cent zinc.	No appreciable effect. Decreased with alloys of low lead and high tin. Frictional force not affected.	Increased at room temperature. No appreciable effect 350° and 600° F.	Tendency to increase toughness at 70°, 350°, and 600° F.	Slightly harder.
05 per cent phosphorus.	Increased in most cases. Frictional force not affected.	Increased at room temperature. Little effect at 350° F. Pronounced decrease at 600° F.	No definite change....	Tendency toward slight increase.
per cent nickel.	Decreased. Frictional force slightly increased.	Marked increase at room temperature less marked at 350° F. Decreased in many cases at 600° F.	Increased with low lead alloys. Decreased with alloys having appreciable amounts of lead.	No appreciable change.
per cent antimony.	Increased in most cases. Frictional force increased at room temperature.	Increased at all temperatures.	Decreased about 30 per cent.	Slightly harder in most cases.

VII. ACKNOWLEDGMENTS

The authors express their indebtedness to H. K. Herschman, associate metallurgist, and to S. J. Rosenberg, assistant metallurgist, for aid in the preparation of this report.

The skillful assistance of L. D. Jones, senior laboratory mechanic, helped materially in the founding of the bronzes.

WASHINGTON, March 7, 1930.

UTTING TESTS WITH CEMENTED TUNGSTEN CARBIDE LATHE TOOLS

By T. G. Digges

ABSTRACT

This investigation was made for the purpose of developing a method of testing mented tungsten carbide lathe tools under heavy duty and to extend to the w cutting material some of the laws originally developed by Taylor and his sociates for cutting with carbon and high-speed steel tools. Relations were termined between the speed, feed, depth of cut, and tool life for a selected form d size of tool. All tests were made dry in cutting 3.5 per cent nickel-steel rgings, heat treated to give tensile strengths within the range of 85,000 to 0,000 lbs./in.^{2} The results are presented in both graphic and tabular forms.

CONTENTS

	Page
I. Introduction	365
II. Previous investigations	366
III. Methods of tests	366
1. Equipment	366
2. Procedure	368
3. Tool failure	370
IV. Effect of cutting speed on tool life	370
V. Effect of feed and depth on the cutting speed	373
VI. General comments on lathe tests	379
VII. Summary and conclusions	382
VIII. Acknowledgments	383

I. INTRODUCTION

Cemented tungsten-carbide tools were first placed on the market on commercial basis in Europe in 1926 and in the United States several ars later. The rapid development of this material during the past ar has made possible its extensive use for tools throughout this untry and abroad. The records of production with these tools have ready shown that this new cutting material will occupy a most portant place in our industrial life.

The experiments described in this report relate primarily to a study lathe-tool performance as affected by the conditions of cutting, such variations in speeds, feeds, and depths, while the composition, the e, and form of the tools and cutting materials were not varied. he investigation was for the purpose of developing a method of test- g tungsten-carbide tools under heavy duty and to establish some of e laws of cutting which define the approximate relations between sts of short duration, which might be made in the laboratory, and ng-time cutting required in practical service. The need of such formation is shown by the large number of inquiries received by e National Bureau of Standards from consumers.

II. PREVIOUS INVESTIGATIONS

No attempt will be made to review the abundant literature published since the introduction of tungsten carbide as a cutting material. The articles published have dealt primarily with outstanding production records and other phases not directly related to the field to be covered. Such data may be used to advantage, and important technical publications containing information on the subject under discussion will be referred to in the individual sections of this report.

III. METHODS OF TESTS

1. EQUIPMENT

A 36-inch heavy-duty engine lathe, driven by a 40 h. p. 220 volt d. c. shunt motor, was selected. (See fig. 1.) A "link belt" chain was used to insure a positive drive. Accurate speed control of the work piece was secured by using the several gearing ratios of the lathe and by changing the speed of the motor with a variable resistance in the field circuit. Experiments showed that it was necessary to increase the rate of speed of the motor in order to prevent excessive slowing down or stalling under heavy loads.

A special tool holder was designed to give ample support to the test tool near the cutting edge. This was firmly clamped in the 4-bolt tool post holder shown in Figure 1.

A "live center" (tailstock) containing a ball bearing and having the form and dimensions shown in Figure 2 was used instead of the customary "dead center." Its insertion required considerable time and labor, but it avoided lubrication troubles common with the "dead center."

A single pointed cutting tool was selected and its form was similar to that commonly employed for heavy-duty roughing work. Its form and dimensions, as shown in Figure 3, consisted of tungsten carbide tips approximately 0.18 inch thick, 0.31 inch wide, and 0.5 inch long, copper brazed on a shank 0.5 inch wide, 1 inch thick, and 7 inches long. The tools had a plane angle of 90° and were ground to 6° front and side clearance, 0° back slope, 14° side slope, 10° back side relief, and the radius of the nose was 0.0625 inch. The edge of the tool from this arc along its cutting edge was ground to a contour of 1.75-inch radius for 0.4375 inch. All tools were hollow ground to a depth of 0.003 to 0.006 inch at approximately 0.25 inch from the cutting edge of the tools. Special grinding wheels of silicon carbide were used for grinding the tools.

The tools used in this investigation were manufactured by the Carboloy Co. (Inc.) by certain sintering operations in which the fine particles of tungsten carbide were cemented firmly together with cobalt, and the material is referred to as cemented tungsten carbide to differentiate it from the cast product. Chemical analyses were made on two lots of tungsten carbide tools that were supplied at different times. Table 1 shows that the tools were quite uniform

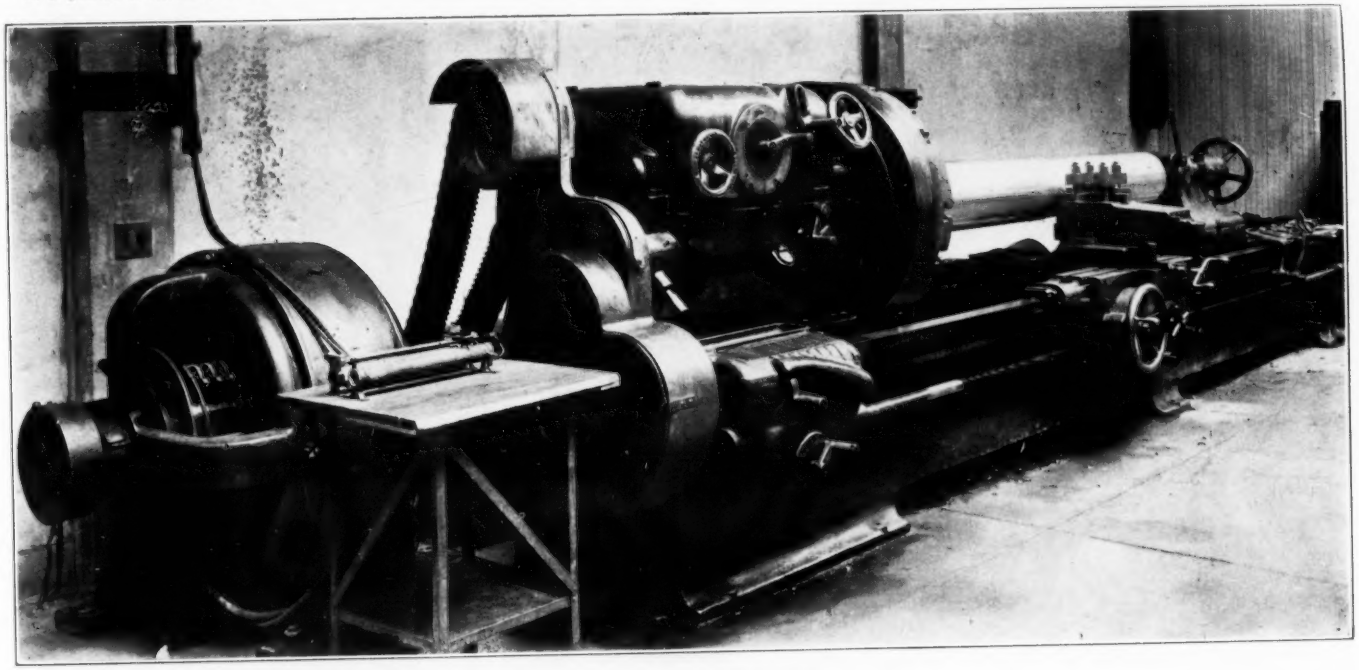


FIGURE 1.—*Lathe used in tool tests*

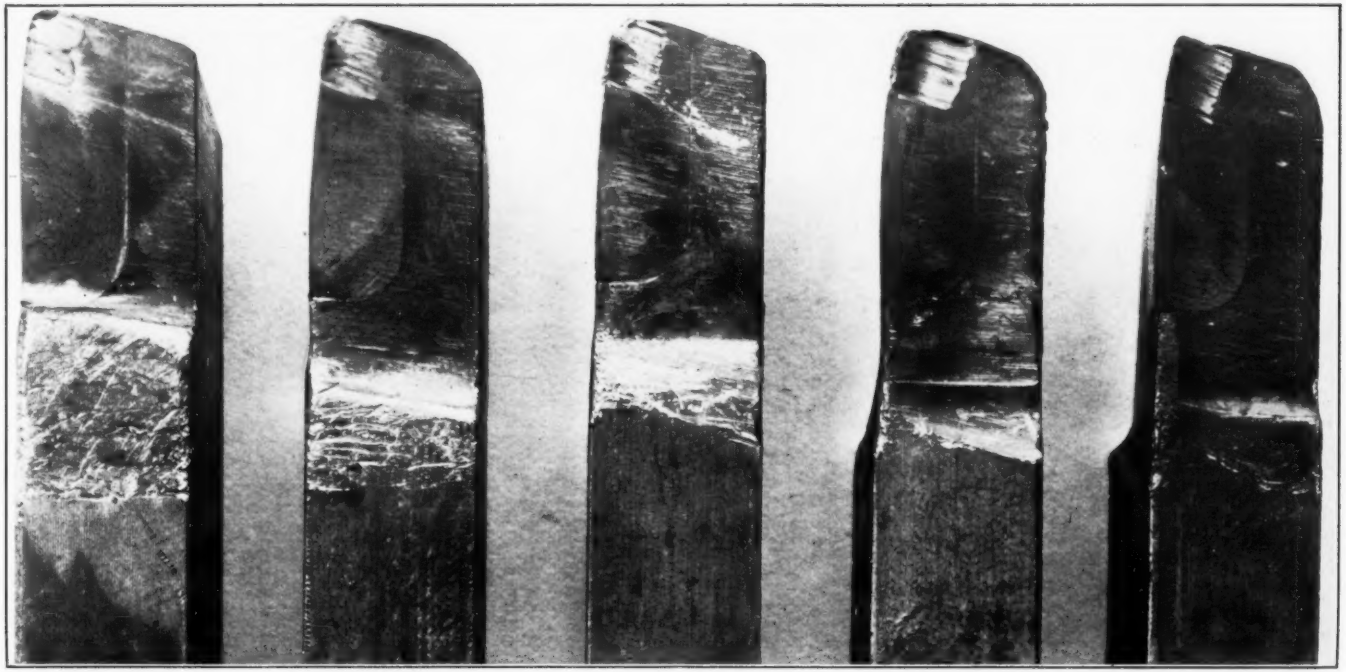


FIGURE 4.—*Depressions worn on top surface of the tools during tests*

All tools had failed except tool shown on extreme left.

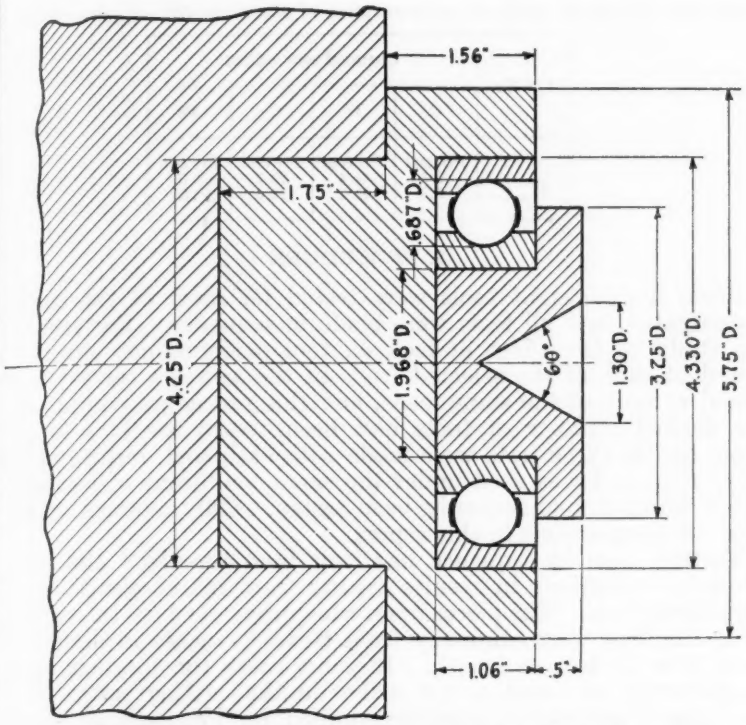


FIGURE 2.—*Type of tail stock center used in lathe tests*

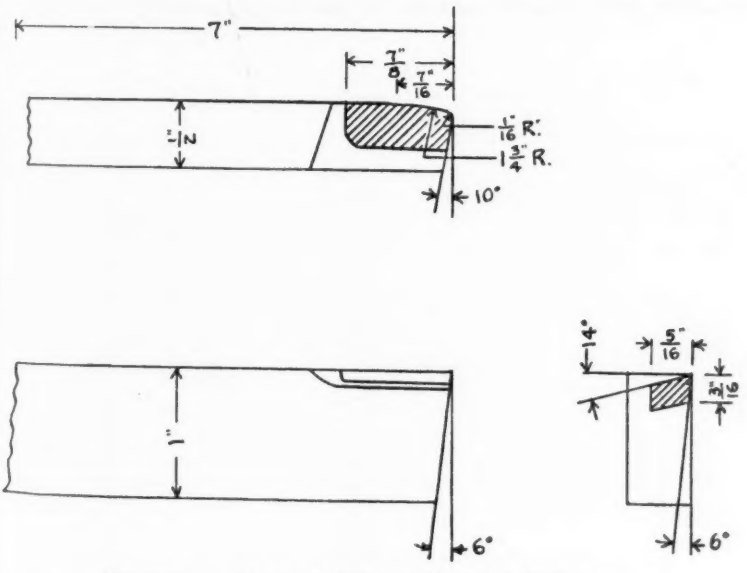


FIGURE 3.—*Size and form of tool used in lathe tests*

TABLE 1.—*Chemical analysis representative of the cemented tungsten-carbide to*

Lot No.	Chemical composition			
	C	W	Co	Fe
	Per cent	*Per cent*	*Per cent*	*Per cent*
1	5.3	81.4	12.7	0.76
2	5.3	81.2	12.6	.66

2. PROCEDURE

From five to eight tools were tested for most of the conditio investigated, and all tests were made in sequence. For example, the study of the effect of feed on tool performance, one tool w tested at each of the selected feeds in the series, a second tool w tested at each of the same feeds, and this procedure continued un the desired number of tools had been tested for each conditio From one to three tests were made with each tool, but no tool aft being reground was used under the same conditions of test as tho under which it had formerly been tested. Only average values a used for comparisons in this report.

Testing tools in sequence has long been practiced and tends minimize variations in results arising from inhomogeneities in th metal being cut. The pieces upon which the cuts were taken, referr to as forgings, were originally from 10 to 12 inches in diameter an from 8 to 10 feet in length. In some cases the forgings were c to diameters as small as 4.5 inches in the cutting tests. Averag mechanical properties were determined on longitudinal specime cut from the forgings so as to represent the average metal remove during cutting. The chemical composition, heat treatment, tensi properties, and Brinell hardness of the forgings are given in Table

Forging No.	Chemical composition [1]							Heat treatment [1]	Proportional limit	Yield point	Tensile strength	Elongation in 2 inches	Reduction of area	Brinell hardness
	C	Mn	P	S	Si	Ni	Cu							
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*		*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*	*Per cent*	*Per cent*	*Number*
44	0.33	0.72	0.044	0.030	0.28	3.29	0.28	1,480° F. held 1½ hours; furnace cooled. 1,530° F. held 3½ hours; and cooled in emulsion.[2] 1,200° F. held 3½ hours; furnace cooled.	81,500	86,500	106,500	26.0	61.3	230
45	.29	.65	.032	.029	.32	3.40	.26	1,540° F. held 3½ hours; cooled in emulsion. 1,220° F., 2½ hours; furnace cooled.	68,500	76,000	100,000	25.5	60.2	202
52	.30	.67	.038	.028	.29	3.39	.24	1,520° F. held 3½ hours; furnace cooled	59,000	60,000	88,800	29.0	53.1	168
53	.30	.61	.026	.037	.26	3.43	.24	do	50,000	51,000	84,200	29.5	47.5	163
54	.31	.68	.042	.035	.31	3.17	.20	1,500° F. held 3½ hours; furnace cooled	51,500	54,000	85,200	31.0	55.0	163
55	.30	.67	.034	.033	.29	3.37	.22	1,650° F. held 3½ hours; air cooled. 1,480° F. held 3½ hours; furnace cooled.	58,000	60,250	95,250	30.5	51.8	180
56 [3]	.26	.57	.041	.035	.15	3.81	.11	1,650° F. cooled in emulsion; 1,560° F. cooled in water; 1,340° F. air cooled.	41,100	49,200	85,600	27.5	55.1	166

[1] Chemical composition and heat treatment data reported by manufacturer.
[2] The emulsion referred to consisted of 5 per cent rapeseed oil, 15 per cent paraffin oil, and 80 per cent water containing 1 per cent sodium carbonate.
[3] Forging No. 56 was hollow bored; hole approximately 5½ inches in diameter; Nos. 44 and 45 were hollow bored; hole 4 inches in diameter.

In making a cutting test the tool was clamped so that its side w at right angles to the longitudinal axis of the forging, with the end the nose on dead center. The lathe was then set at the desired fee the tool at the required depth, and the speed of the lathe adjusted give the forging the desired peripheral speed. The tool was fed b hand until the desired cut was reached, after which the automatic fe was thrown in and the time recorded. The speed of the forgi decreased when cutting began, but was quickly adjusted to bring back to its original value. Before starting any test, care was take to remove any glazed surface on the forging caused by the breakdow of the previous tool or any particles of the tool that might hav become embedded in the forging.

All tests were run dry, and the cutting speed, feed, and depth cut were varied, depending upon the purpose of each series of tests.

3. TOOL FAILURE

A groove was formed on the top surface of the tool near the "leadi edge" soon after the tool started to cut. This depression becam greater as the test progressed until a condition was finally reache when the wear was sufficient to cause a small section to chip or bre out of the working portion of the tool. This "end point" usual resulted in a glazed surface on the test forging and was often accom panied by a splitting of the chip which gave an additional indicati of tool failure. Thus, there was a very definite end point and one th could be recognized without much difficulty. In some of the exper ments, especially those of the most severe conditions of cutting, th end point was often quickly followed by, if not simultaneous wit tool breakage which would leave doubt as to the time of tool failur Such doubtful tests were discarded in these experiments. In som cases it would have been possible to continue to cut after the describe condition was reached, but only at the expense of badly broken tool All cutting results given in this report were obtained by the "end point" method described. The wear on the top and front surfaces the tools at the time of failure is illustrated in Figures 4 and 5.

The appearance of the forging at the time of failure of the tungsten carbide tools was very similar to the appearance of a forging when high-speed steel tool fails under the so-called "lathe breakdown test." A glazed surface was produced on the forging at the bottom of th cut at the time of tool failure as is shown in Figure 6.

IV. EFFECTS OF CUTTING SPEED ON TOOL LIFE

It is a well-known fact that the cutting speed of a high-speed ste lathe tool is dependent upon the quality, composition, and heat trea ment of the tool and on the properties of the metal cut as well as upo the size and form of tool, feed, and depth of cut. It appeared reason able to assume that the cutting speed of cemented tungsten-carbid lathe tools should depend upon approximately the same variables high-speed steel tools, and it was upon this basis that the experimen were performed.

The results of tests at different speeds with a feed of 0.031 inch p revolution and depth of 0.1875 inch are summarized in Table 3 an Figure 7. Figure 7 shows that there was a continuous increase in th

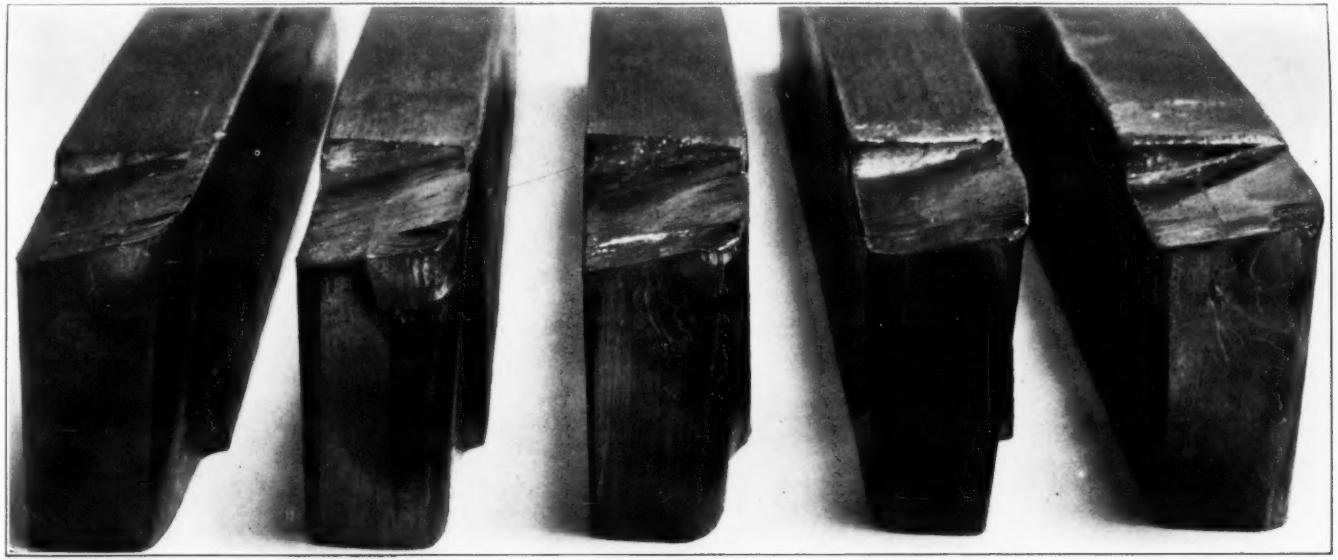


FIGURE 5.—*Wear on front of tools during test*

All tools had failed except tool shown on extreme left.

FIGURE 6.—*Appearance of test forging at time of tool failure*

Note the glaze at the bottom of the cut.

life of tungsten-carbide tools as the cutting speed was decreased. Within the life range of 9 to 156 minutes the experimental results may be represented by the empirical equation

$$VT^n = c \tag{1}$$

in which

V = the cutting speed in feet per minute.

T = the tool life in minutes.

c = a constant which is dependent upon the cutting conditions other than speed. It should vary with the form and size of tools, material cut, nature of tools, feed, and depth of cut.

n = constant.

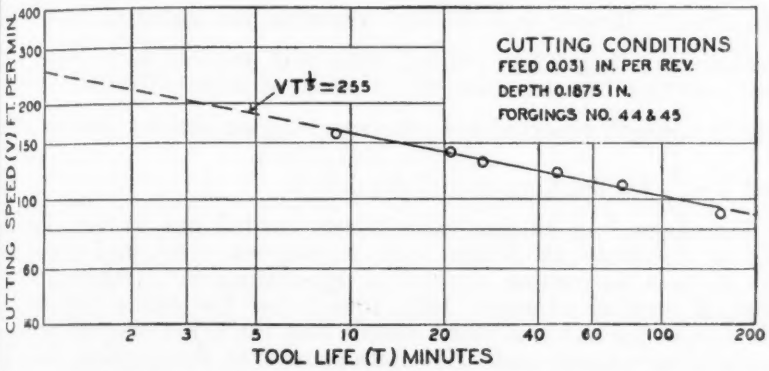


FIGURE 7.—*Summary of lathe tests showing that cutting speed of cemented tungsten carbide tools varies inversely as one-fifth power of their life*

[1] Tests were made "dry" with form and size of tool shown in Figure 3. Properties of test forgings given in Table 2. Note that logarithemetic coordinates are used

TABLE 3.—*Effect of speed on performance of cemented tungsten-carbide lathe tools*

Cutting conditions				Number of tests	Average tool life	Calculated cutting speed [1]	Average power required in cutting
Forging No.[2]	Speed	Feed	Depth				
	Ft./min.	*In./rev.*	*Inch*		*Min.*	*Ft./min.*	*kw.*
44 and 45	90	0.031	0.1875	5	155.9	93	4.1
	110	.031	.1875	6	74.9	108	5.4
	120	.031	.1875	6	45.9	119	5.5
	130	.031	.1875	3	26.7	132	6.2
	140	.031	.1875	6	21.2	139	6.4
	160	.031	.1875	5	9.0	164	6.8

[1] Computed by means of equation $VT^n = C$ with $n = \frac{1}{5}$ and $c = 255$.

[2] All tests were run dry with the size and form of tool shown in Figure 3. See Table 2 for properties of forgings.

Taylor [1] found the effect of cutting speed on the tool life of high-speed steels could be represented by equation (1). This empirical relationship between tool life and cutting speed with high-speed steel tools was recently confirmed by the Lathe Tool Research

[1] F. W. Taylor, On the Art of Cutting Metals, Trans. A. S. M. E., 28, p. 31; 1907.

Committee [2] and by tests conducted at the National Bureau o Standards,[3] [4] and by Ripper and Burley. [5]

Taylor [6] reported cutting tests on carbon steels having a tensil strength of about 70,000 lbs./in.^{2} with tools of definite size an shape made from steel containing about 1.9 per cent carbon, 8 per cent tungsten, and 2 per cent chromium. He found the valu $n=\frac{1}{8}$ and $c=90$, but stated:

> We have made a number of experiments with different qualities of steel an find that approximately the same relation exists between the duration of cu and cutting speed for steels of different degrees of hardness. This statemen however, does not apply to cast iron.

Not all investigations have confirmed Taylor's value of the expo nent "n." Ripper and Burley [7] reported the value of $n=\frac{1}{12}$ an French and Digges [8] in cutting tests with modern high-speed ste tools cutting 3½ per cent nickel steel of about 100,000 lbs./in. tensile strength reported $n=\frac{1}{7}$ for roughing conditions (heavy duty and $n=\frac{1}{10}$ for finishing cuts (light duty).

Schlesinger,[9] in cutting experiments carried out at the Techno logical Institute at Berlin with high-speed steel and superhar metal tools in cutting a steel of approximately 100,000 lbs./in. (Brinell number of about 190), found that the cutting speed to life curves for the superhard metals had the same characteristic s those of high-speed steel. His data show that the relations betwee tool life and cutting speed for sintered tungsten-carbide tools, whe the cross section of the chip was 0.158 by 0.039 inch, could be closel represented by equation (1) when $n=\frac{1}{4.6}$. In another set of exper ments which appear to have been carried out under the same te conditions it was found that $n=\frac{1}{7.1}$. With high-speed steel tools was found to be equal to about $\frac{1}{6.3}$, which is in close agreement to th value reported by the Bureau of Standards for roughing tests.

Examination of the results summarized in Figure 7 shows th the experimental values obtained for sintered tungsten carbid tools were approximately represented by equation (1) with $n=$ Therefore, the equation

$$VT^{\frac{1}{8}}=c \qquad (2$$

[2] Department of scientific and industrial research, Manchester Associa'ion of Engineers. The 19 Report of the Lathe Tool Research Committee, published by His Majesty's Stationery Office, London.
[3] H. J. French and T. G. Digges, Rough Turning with Particular Reference to the Steel Cut, Tra A. S. M. E., **48**, p. 533; 1926.
[4] H. J. French and T. G. Digges, Turning with Shallow Cuts at High Speeds, B. S. Jour. Research, p. 829; 1929.
[5] W. Ripper and G. W. Burley, Cutting Power of Lathe Turning Tools, Proc. Inst. Mech. Engrs., Pt 3 and 4, p. 1967; 1913.
[6] See footnote 1, p. 371.
[7] See footnote 5.
[8] See footnotes 3 and 4.
[9] George Schlesinger, German Practice with Tungsten-Carbide Tools, Am. Machinist, **71**, p. 37; 1929.

was used for all computations in this report involving the relation between the cutting speed and tool life. There was a close concordance between the experimental results and the calculated values and equation (2) should be sufficiently accurate for all practicable purposes except for extrapolating for very long tool life from tests of short duration. It is of interest to note that this law as originally developed by Taylor and his coworkers was confirmed with the cemented tungsten carbide lathe tools for duration of cut between 9 and 156 minutes under conditions widely different from those of Taylor's experiments.

Equation (2), which expresses the relation between tool life and cutting speed, is represented graphically by straight lines when logarithmetic rectangular coordinates are used. The chart reproduced in Figure 8 is of a convenient form for computing the life of tools at various speeds and makes it simpler to interpolate between the values of the constant, c, shown on the chart, than would be the case with the curves obtained with Cartesian coordinates.

V. EFFECT OF FEED AND DEPTH OF CUT ON THE CUTTING SPEED

It is not practicable to select a single cutting speed for lathe-tool testing varying widely in either feed or depth of cut because of the expense of the large amount of material that would be involved and the time required to make such test. The cutting speed has already been shown to have an empirical relation to the tool life at a given feed and depth so that in the study of the effects of feed and depth on tool performance the cutting speed was also varied. In general, cutting speeds giving an average tool life from 10 to 30 minutes were selected and then the cutting speeds for the desired tool life were computed by means of equation (2).

Two series of tests were made with the cemented tungsten-carbide tools in order to establish the relations between the cutting speed, feed, and depth of cut. One was made with a constant depth of cut of 0.1875 inch and feeds ranging from 0.031 to 0.096 inch per revolution, and the other with a constant feed of 0.031 inch per revolution and depths of cut ranging from 0.125 to 0.5625 inch.

The results of the tests made with a constant depth of cut and variable feeds are given in Table 4, and the cutting speeds for a 90-minute tool life with the different feeds used in the experiments are summarized in Figure 9. As shown in Figure 9, the relation between the cutting speed and the feed for a given tool life at a constant depth of cut may be represented approximately by the relation

$$VF^m = c_1 \qquad (3)$$

in which

V = cutting speed in feet per minute for a selected tool life.
F = feed in inches per revolution.
c_1 = constant.
m = constant.

When operating with cutting speeds for a selected 90-minute tool life at a 0.1875-inch depth of cut in cutting 3.5 per cent nickel steel forging having a tensile strength in the neighborhood of 85,000

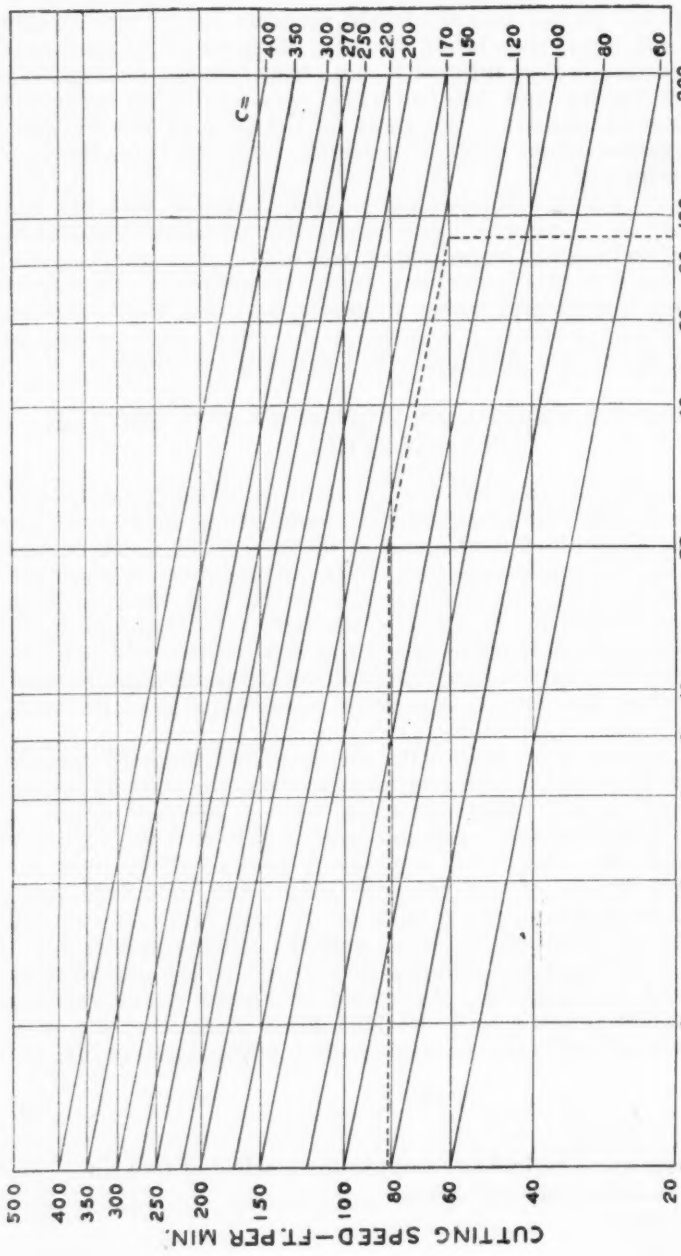


FIGURE 8.—*Chart giving relation between cutting speed and tool life*

Lines drawn according to equation $VT^{\frac{1}{n}}=C$ in which V=cutting speed, T=tool life, C=constant, n=constant

CUTTING SPEED FOR 90 MIN LIFE (V) FT/MIN.

lbs./in.^{2}, the exponent m was found to be 0.58, with c_1 equal to 16.6. Substituting these results in equation (3), we have

$$VF^{0.58} = 16.6 \qquad (4)$$

The detailed results as recorded in Table 4 show a surprisingly close agreement between the individual tool performances. In a majority of the tests this variation was no greater than that ordinarily found when testing high-speed steel lathe tools under heavy duty.

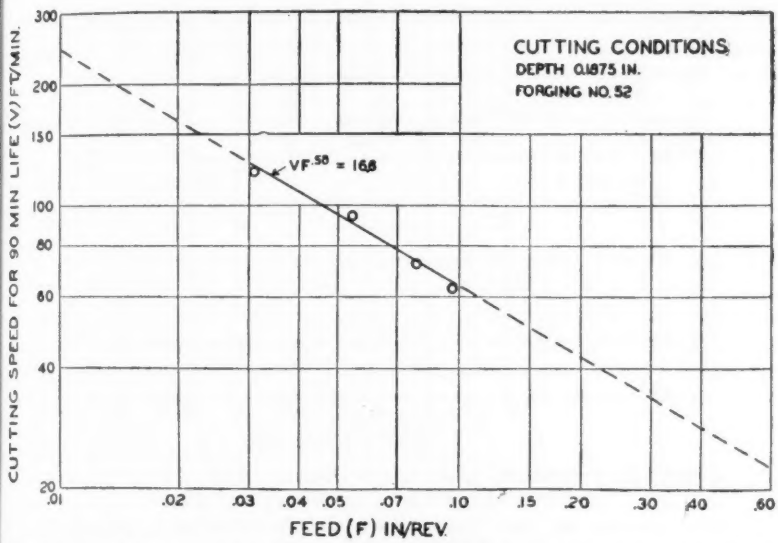


FIGURE 9.—*Summary of lathe tests showing effect of feed on cutting speed for a 90-minute tool life*

Tests were made "dry" with form and size of tool shown in Figure 3. Properties of forging given in Table 2

Line drawn according to equation

$$VF^{.58} = 16.6$$

in which
V=cutting speed for 90-minute tool life, feet per minute.
F=feed, inch per revolution.

TABLE 4.—*Effect of feed on performance of cemented tungsten carbide lathe tools*

[All tests were run dry with the size and form of tool shown in fig. 3]

Cutting conditions				Tool life								Average power required in cutting	Cutting[1] speed for 90-minute tool life
Forging No.[2]	Speed	Feed	Depth	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Average		
	Ft./min.	*In./rev.*	*Inch*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*kw.*	*Ft./min.*
52	160	0.031	0.1875	30.6	11.5	21.2	20.8	20.8	27.3	25.0	22.5	5.5	121
52	120	.054	.1875	26.9	31.0	27.3	40.5	12.2	26.4	[3]	27.4	7.1	94
52	105	.078	.1875	23.3	8.0	12.1	16.0	[3]	12.7	12.6	14.1	8.5	72
52	90	.096	.1875	16.7	14.8	19.3	[3]	9.1	16.7	[3]	15.3	9.3	63

[1] Computed from average tool life by means of equation $VT^{\frac{1}{4}}=c$.
[2] See Table 2 for properties of forging.
[3] Tool broke.

The results of the cutting tests made with a constant feed and variable depths are given in Table 5. The cutting speeds for a 90-minute tool life with the different depths used in the experiments are summarized in Figure 10. The results show that there was a

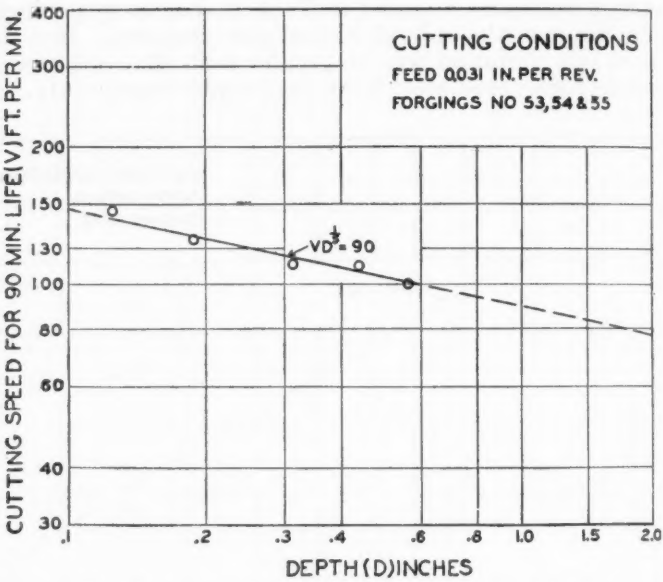


FIGURE 10.—*Summary of lathe tests showing effect of depth of cut on cutting speed for a 90-minute tool life*

Tests were made "dry" with form and size of tool shown in Figure 3. Properties of forgings given in Table 2

Line drawn according to equation

$$VD^{\frac{1}{2}}=90$$

in which

V=cutting speed for 90-minute life, feet per minute.
D=depth of cut, inches.

continuous increase in the cutting speed with decrease in depth of cut and that the relation between the cutting speed and depth of cut with a constant feed and given tool life may be represented by the equation

$$VD^p=c_2 \tag{5}$$

in which

V = cutting speed in feet per minute for a selected tool life.
D = depth of cut in inches.
c_2 = constant.
p = constant.

p was found to be equal to 0.2 and c_2 was equal to 90, for a 90-minute tool life, and with a feed of 0.031 inch per revolution and depths of cut varying from 0.125 to 0.5625 inch. Substituting these results in equation (5) we have

$$VD^{0.2}=90 \tag{6}$$

An examination of Figure 10 shows that there was a close agreement between the experimental and calculated values over a wide range of depths of cut.

As already stated, the cutting speed for a given tool life is dependent upon the quality and composition of the tool, the properties of the metal cut, size and form of tool, feed, and depth of cut.

TABLE 5.—*Effect of depth of cut on performance of cemented tungsten carbide lathe tools*

[All tests were run dry with the size and form of tool shown in fig. 3]

Cutting conditions				Number of tests	Average tool life	Average power required in cutting	Cutting speed [1] for 90-minute tool life
Forging No.[2]	Speed	Feed	Depth				
	Ft./min.	*In./rev.*	*Inch*		*Minutes*	*kw.*	*Ft./min.*
53, 54, and 55	200	0.031	1/8	8	17.7	5.7	144
	180	.031	3/16	8	15.1	7.2	126
	160	.031	5/16	8	14.4	11.8	111
	150	.031	7/16	7	18.5	16.6	109
	140	.031	9/16	7	16.5	20.6	100

[1] Computed from the average tool life by means of equation $VT^{1/5}=c$.
[2] See Table 2 for properties of forgings.

In these experiments the quality and composition of the tools, size and form of tools, and the metal cut were kept as near constant as possible, so that the cutting speed for a given tool life was dependent only upon the feed and depth of cut.

From equations (4) and (6) for a 90-minute tool life we have

$$VF^{0.58}D^{0.2}=K=12 \tag{7}$$

or

$$V=\frac{K}{F^{0.58}D^{0.2}}=\frac{12}{F^{0.58}D^{0.2}} \tag{8}$$

The equations given in this report check experimental values closely, and can be used as the basis for computing speeds for a selected tool life under varying conditions, provided the size, form, quality, and composition of tools and the type of cutting material herein described are used. If the tool life is known at some one speed, feed, and depth of cut, these computations require only the use of equations (2) and (7). The computations necessary in applying equations (2) and (7) are, however, tedious because of the form of equation (7), and to avoid these computations the chart reproduced in Figure 11 was constructed. This chart is adopted for the reading of the various cutting speeds permitting a 90-minute tool life with various combinations of feeds and depth of cut. With the logarithmetic rectangular coordinates used for depth of cut and feed, the cutting speed (V) (shown on chart, fig. 11) for 90-minute tool life is represented by straight lines.

In using this chart, find the intersection of the desired feed and depth coordinates. This point of intersection will usually fall between the sloping lines representing the cutting speed. This value will give the approximate cutting speed (V) for a tool life of 90 minutes. The cutting speed for a tool life within the range of 1 to 200 minutes may be obtained from the charts reproduced in Figures 11 and 8 or by equations (7) and (2),

For example, if it is required to compute the cutting speed for a 90-minute tool life with a feed of 0.08 inch per revolution and 0.5 inch depth of cut, from Figure 11 it will be seen that the 0.08 inch per revolution feed and 0.5-inch depth coordinates intersect at the speed line corresponding to 60 feet per minute. Now, if the cutting speed for 20-minute tool life with the same feed and depth of cut is desired, we have the value of 81 as given by the chart shown in Figure 8. This latter value is obtained by finding the intersection of the abscissa representing a tool life of 90 minutes (follow the dotted line in fig. 8) with the ordinate representing a cutting speed of 60 feet per minute, then by interpolating by following the straight line (shown in fig. 8 as $c=150$) until this line intersects the abscissa representing a tool life of 20 minutes.

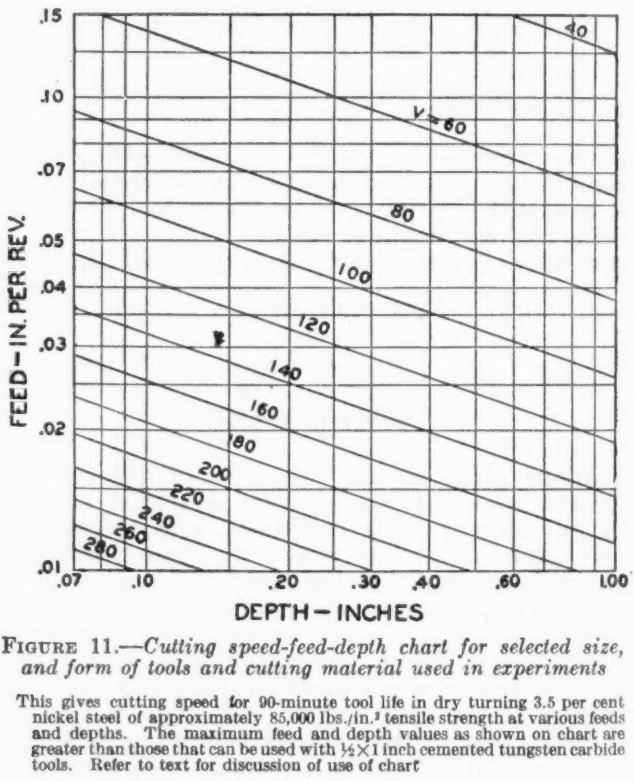


FIGURE 11.—*Cutting speed-feed-depth chart for selected size, and form of tools and cutting material used in experiments*

This gives cutting speed for 90-minute tool life in dry turning 3.5 per cent nickel steel of approximately 85,000 lbs./in.² tensile strength at various feeds and depths. The maximum feed and depth values as shown on chart are greater than those that can be used with ½×1 inch cemented tungsten carbide tools. Refer to text for discussion of use of chart

Figure 11 was constructed with the lines representing the permissible cutting speeds for 90-minute tool life, ranging from 40 to 280 feet per minute at intervals of 20 feet per minute. Cutting speeds other than those shown on the chart for a 90-minute tool life may be estimated with a reasonable degree of accuracy by extrapolation.

The limits of the values for feed and depth as given in Figure 11 are in excess of those that can be used with 0.5 by 1 inch cemented tungsten-carbide tools. However, it is possible to use a wide range of feeds and depths of cut with this size tool. This chart should

also be applicable (with modifications) to larger tools than those used in the experiments.

As already stated, equation (7) does not take into consideration changes in size and form of tools and variations in materials cut. The need of such tests becomes immediately apparent in order to extend the relations between the relatively short time laboratory test of this new cutting material to its wide field of industrial work.

As shown by equation (7), the cutting speed is not affected equally by changes in feed and depth of cut. A higher cutting speed is associated with a deep cut and fine feed than with a corresponding combination of coarse feed and shallow cut. Equations (2) and (6) show that the exponents, n and p, expressing the relation between cutting speed and tool life and the cutting speed and depth of cut are equal.

VI. GENERAL COMMENTS ON THE LATHE TESTS

Despite the fact that cemented tungsten carbide contains appreciable proportions of cobalt, it is a relatively brittle material and for this reason the cutting tools must be well supported. For these tests the carbide tips were joined to the tool shank by copper brazing in a hydrogen atmosphere. Hoyt [10] stated:

> It has been found that tungsten-carbide tips which are rigidly welded to the shank are only too apt to come off, either directly after the tool is made, or after being put in service. This is due to thermal stresses which are set up by temperature changes and differences in the coefficients of expansion of the carbide and the steel. This circumstance accounts for the popularity of copper brazing, because here the thin layer of copper affords a soft cushion which absorbs such stresses without transmitting them to the carbide tip. On the other hand, copper softens at elevated temperatures, so that it is necessary, in the design of the tool, to remove the joint far enough away from the cutting edge so that it does not get dangerously hot during operation.

This method of attaching the carbide tip was satisfactory for most of the conditions used in the cutting tests, although premature failure in several tests resulted because of the rupture of this bond.

The heaviest cuts used with the 0.5 by 1 inch tools were probably greater than those that could be used in ordinary shop practice where cost, due to tool breakage, becomes important. The carbide tips of the tools were reduced in size by grinding and weakened accordingly so that most of the tool breakage was confined to the heaviest cuts with tools that had been reground. The test showed that the tools could be used under relatively heavy duty provided they were properly supported and not subjected to vibration.

The forces on a lathe tool, while cutting, are practically independent of the cutting speed and are dependent upon the cross section of the chip. It is evident from this principle that tungsten-carbide tools should be used at relatively high speeds and for light cuts in order to keep tool breakage at a minimum. As shown by equation (2), the cutting speed varies as the one-fifth power of the tool life. This indicates that a small change in cutting speed causes a correspondingly large change in the tool life so that the higher cutting speeds are obtained only at the expense of shorter tool life. The most economical cutting conditions must therefore be a com-

[10] S. L. Hoyt, Tungsten Carbide Tools Most Renumerative of Production Jobs, Iron Age, **124**, p. 1173; 1929.

promise between several factors such as increase in cutting speed with decrease in tool life and tool breakage in order to remove the maximum amount of metal in the minimum time at the least cost.

Some idea of the relation between the cutting speeds associated with tungsten-carbide tools and high-speed steel tools may be obtained from the cutting speed—tool life curves reproduced in Figure 12. Attention is directed to the fact that the two curves were not made under identical conditions of cutting, and only a general comparison can be made from these results. For example, the tungsten-carbide tools were larger than those used in the high-speed steel experiments and the tool angles were different for the two types of tools.

The high-speed steel tools were of the 18 per cent tungsten type, quenched in oil from 2,400° F. and tempered at 1,100° F. These tools were 0.25 by 0.5 inch in size, and were ground to a front and

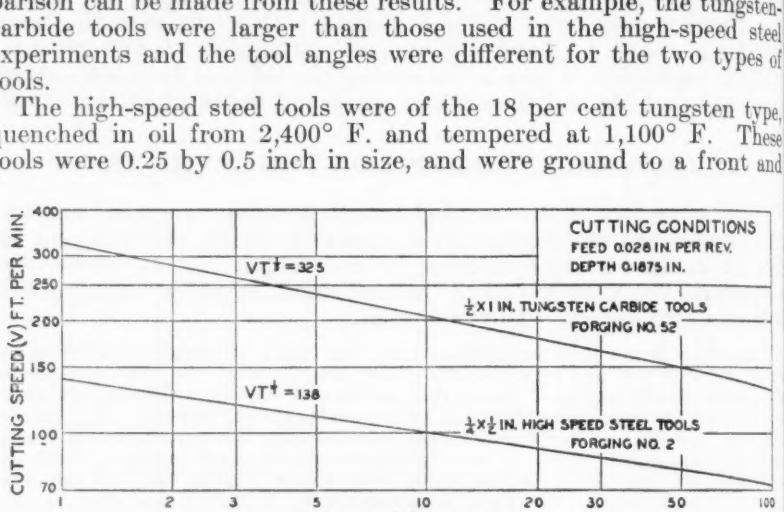


FIGURE 12.—*Summary of relation between cutting speed and tool life with tungsten carbide and high speed steel lathe tools*

Tests were run "dry" with the size and form of tools shown in report. Properties of forgings given in Table 2

For cemented tungsten carbide tools, line drawn according to equation

$$VT^{\frac{1}{4}}=325$$

For high-speed steel tools line drawn according to equation

$$VT^{\frac{1}{4}}=138$$

in which

V=cutting speed, feet per minute.
T=tool life, minutes.

side clearance of 6°, side slope of 8°, back slope of 14°, and a nose radius of 0.125 inch. The cutting materials (as shown in Table 2) had approximately the same chemical and physical properties, but as already pointed out, it does not necessarily follow that the two forgings have the same cutting properties. Both forgings were of the 3.5 per cent nickel type, heat treated to give a tensile strength of about 85,000 lbs./in.^{2}

Figure 12 shows that considerably higher cutting speeds (under certain conditions) were obtained with the tungsten-carbide tools than with the high-speed steel tools. Also, the slope of the straight lines representing the relations between cutting speed and tool life with the logarithmetic system of coordinates were different for the two types of tools. The slope of the curves obtained with the tungsten-carbide tools was greater than that obtained with the high-

speed steel tools. This means that the two curves tend to approach each other, and the differences between the cutting speeds of the two materials decrease with increase in tool life. If these curves are extrapolated to an extremely long tool life, then the curves will cross and the high-speed steel tools would show higher cutting speeds than the tungsten-carbide tools. However, such long time cutting can not be extrapolated with any degree of accuracy from the present empirical equations, and it is also doubtful if cutting conditions resulting in such long tool life would ever be practicable in modern shops from an economical standpoint.

Cemented tungsten-carbide tools have the property of red hardness to a remarkable degree. This property permits higher cutting speeds under certain conditions than is the case with the best tool steels.

While the tungsten-carbide tools were considerably superior to those of high-speed steel in cutting 3.5 per cent nickel-steel forgings of about 85,000 lbs./in.^{2} tensile strength, it does not follow that the same degree of superiority will be obtained under widely different cutting conditions, especially where heavy feeds and deep cuts are used. Therefore, it is necessary to know exactly the cutting conditions in order to make a comparison of the two types of tools.

No direct indication of the performance of the tungsten-carbide tools could be detected by the types of chips produced in the lathe tests. In general, the chips came off in very long ribbons during the first part of the cut and then became shorter with more curl as the cutting time increased. A short time before tool failure the chips were approximately 0.5 to 1 inch in length. While these chips were characteristic for some of the conditions employed, especially with tools tested on forgings No. 52, they were not characteristic of the tools tested under conditions of varying depths of cut on forgings Nos. 54 and 55. In the latter case the long chips often continued until tool failure.

The power required in cutting was determined in all of the lathe tests with tungsten-carbide tools and was determined at frequent intervals throughout the life of the lathe tools, so that only average values were obtained. The instruments used, however, did not permit determinations of the fluctuations or the maximum momentary power consumption. The results given in Table 3 show that at constant feed and depth of cut the power was approximately proportional to the cutting speed. The exact relations between the feed and depth of cut and the power consumed can not be established at this time. The results given in Tables 4 and 5 show that there was an increase in the power with increase in feed or depth. However, as already pointed out, the feed and depth experiments were not made at a constant speed, so that the magnitude of the changes in power due to changes in feed or depth can not be established from the limited number of tests made. The power determinations are included with the test results in order to show that it is necessary to have machines equipped with powerful driving units in order to utilize the full capacity of tungsten-carbide tools.

VII. SUMMARY AND CONCLUSIONS

1. The primary object of this investigation was to develop a method of testing tungsten-carbide lathe tools under heavy duty and to extend to the new cutting material some of the empirical laws originally developed by Taylor and his associates for tough turning with carbon and high-speed steel tools.

2. The so-called lathe breakdown test for high-speed steels was found applicable for testing cemented tungsten-carbide tools under heavy duty.

3. The characteristics of the cutting speed—tool life curves for tungsten carbide tools—were similar to those of high-speed steel tools.

4. In dry rough turning 3.5 per cent nickel steel of about 105,000 lbs./in.^{2} tensile strength, with a constant feed, death of cut, tool size, and form, the relation between cutting speed and tool life within the life range of 9 to 156 minutes may be represented by the empirical equation

$$VT^n = c$$

where

V = the cutting speed in feet per minute.
T = the tool life in minutes.
n = constant = $\frac{1}{5}$
c = constant which is dependent upon the conditions of cutting. It will vary with the form and size of tools, materials cut, feed and depth of cut.

5. For a given area of cut, higher cutting speeds are obtained with deep cuts and fine feeds (within limits) than with shallow cuts and coarse feeds.

6. The relation between cutting speed, feed, and depth of cut in terms of the experimental conditions may be represented by the empirical equation

$$VF^{0.58}D^{0.2} = K = 12$$

in which

V = the cutting speed for a selected tool life.
F = feed in inches per revolution.
D = depth of cut in inches.
K = constant = 12 for the experimental conditions.

7. Higher cutting speeds are obtained with cemented tungsten-carbide tools under certain conditions of cutting than with high-speed steel tools.

8. Cemented tungsten-carbide tools are brittle, but when properly supported will produce excellent results under certain cutting conditions.

9. High cutting speeds with relatively fine cuts are more favorable to the successful application of tungsten-carbide tools than heavy cuts at slower speeds.

10. Machines capable of operating at high speeds with powerful driving units are necessary to utilize the full cutting capacity of cemented tungsten-carbide tools.

VIII. ACKNOWLEDGMENTS

The writer acknowledges the assistance and suggestions of Dr. S. L. Hoyt and W. E. Smith. The Carboloy Co. (Inc.) donated all tungsten-carbide test tools and the majority of test forgings.

Grateful acknowledgment is also due to Dr. R. L. Dowdell, senior metallurgist, for his aid and constructive suggestions in the presentation of the test data, to W. V. Magruder, jr., laboratory aid, and C. F. Raab, machinist, formerly of the Bureau of Standards, for their assistance in assembling the equipment and for carrying out many of the tests.

WASHINGTON, March 8, 1930.

HEAT TRANSFER THROUGH METAL-INCLOSED INSULATION

By M. S. Van Dusen

ABSTRACT

The paper gives a mathematical treatment of the problem of heat transfer through an insulated metal-inclosed panel, such as a sheet-metal door, consisting essentially of a sheet-metal box filled with insulating material. The treatment is necessarily approximate, but the approximations involved are accurate enough for practical purposes. The effect of a solid metal thermal short circuit, such as a supporting member extending from one metal surface to the other, is also considered. Calculations and graphs are included, showing the relative magnitude of the heat transfer by metallic induction in a number of cases which might be considered in the design of this type of construction. It is shown that the increase in heat transfer through a metal-inclosed panel due to the presence of the metal may be as high as 100 per cent in many cases which might be considered in practical design.

CONTENTS

	Page
I. Introduction	385
II. Mathematical theory	385
III. Effect of a small thermal short circuit in the central portion of a panel	390
IV. Appendix I. Metal edges	392
V. Appendix II. Thermal short circuit	395

I. INTRODUCTION

The question of heat transfer through what might be termed an insulated panel, consisting of a slab of insulating material completely inclosed by sheet metal, the dimensions of the sides being large in comparison with the thickness of the panel, has been raised on a number of occasions, but the effect of metallic conduction around the edges of such a panel apparently has been a matter of conjecture. Insulated construction of this kind has many points in its favor, the principal one being that the insulating material is effectively sealed against moisture for a long period. The importance of this in refrigerator or cold-storage construction is well known. It is evident that definite information regarding the edge effect will be useful in the design of insulated construction of the metal-inclosed type. This paper offers a solution of the problem; necessarily approximate, but accurate enough for practical purposes.

II. MATHEMATICAL THEORY

It does not appear necessary to give the detailed mathematical analysis at this point,[1] but it will be of interest to state the assumptions made and to indicate the general line of reasoning. Consider

[1] Detailed analysis is given in the appendixes.

a cross section (parallel to the general direction of heat flow) of an "insulated panel," together with adjacent ones, as shown by Figure 1.

The warm surface of the panel receives heat from the warmer air (at temperature θ_2) in contact with it, part of which is conducted through the insulation and part through the metal around the edges. Since the thermal conductivity of the metal is much greater than that of the insulating material, the temperature at the point A will be lower than that at C, and the temperature at B will be higher than that at D. By symmetry, however, the temperature on the plane EF will be the mean between θ_2 and θ_1, neglecting unimportant variations with temperature of thermal conductivity and surface resistance. Bearing this picture in mind, the following assumptions have been made:

1. Heat transfer between the warm air and the warm surface of the panel is proportional to the temperature difference between the warm air and the metal surface.

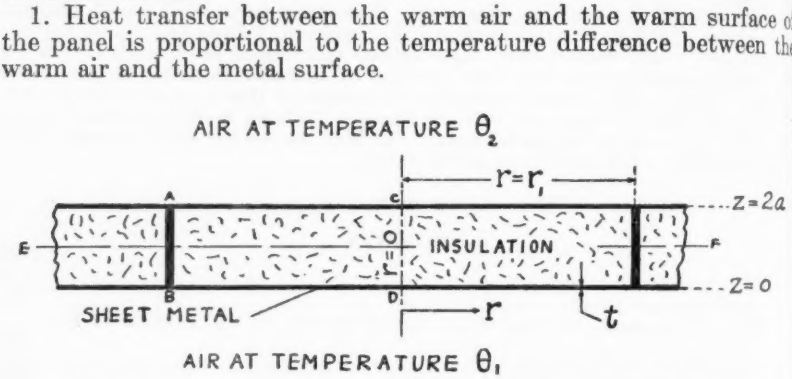


FIGURE 1.—*Cross section of circular panel with complete metal inclosure*

2. Heat transfer at any point between the warm metal surface and the insulation is proportional to the temperature difference between the metal at that point and the middle plane EF. Subsequent numerical calculations show that this approximation is accurate enough for practical purposes.

3. The sheet metal is relatively so thin and is such a good conductor compared to the insulation that temperature gradients in the metal perpendicular to its surface are negligible.

4. That portion of the metal between A and B suffers no net gain or loss of heat. This assumption is justified by considerations of symmetry.

5. Similar assumptions obviously apply to the cold metal surface.

It will be evident that the presence of the metal increases the heat transfer, but at the same time the heat transfer through the insulating material is less than it would have been were there no metal present. The net increase in heat transfer is the difference between these two effects.

Even with the simplifying assumptions enumerated above, the rigorous solution for a rectangular panel appears to be extremely complex. The solutions for a panel having a very large area so that corner effects can be neglected, and for a circular panel, however, are comparatively easy to obtain. In the range of practical cases the difference between these two solutions is so small that the uncertainty

in their use for calculations applied to a rectangular panel is of no practical importance. The solution for a circular panel will be used in most of the numerical calculations, since it represents the closer approximation.

The following notation will be used:

K = thermal conductivity of metal.
t = thickness of metal.
$2a$ = thickness of insulation.
k = thermal conductivity of insulating material.
h = surface conductance per unit area between air and metal.
A = area of panel.
P = perimeter of panel.
I = net percentage increase in heat transfer due to presence of metal edges (basis, heat transfer without metal edges).
T = transmittance of panel (total rate of heat transfer per unit temperature difference between air on both sides).

For a circular panel:

$$I=\frac{Pah}{Ak\left[\frac{ah+k}{Kt}+\gamma\sqrt{\frac{ah+k}{aKt}}\right]} \tag{1}$$[2]

where

$$\gamma=\frac{J_0\left(i\frac{2A}{P}\sqrt{\frac{ah+k}{aKt}}\right)}{-iJ_1\left(i\frac{2A}{P}\sqrt{\frac{ah+k}{aKt}}\right)} \tag{2}$$

The quantity γ is a real function of the Bessel's functions J_0 and J_1 with pure imaginary arguments, and approaches unity with increasing size of panel. In the limit, therefore, equation (1) reduces to

$$I=\frac{Pah}{Ak\left[\frac{ah+k}{Kt}+\sqrt{\frac{ah+k}{aKt}}\right]} \tag{3}$$

Equation (3) can also be obtained by a direct method not involving the use of Bessel's cylindrical functions.[3] The differences between equation (3) and equation (1) are only a few per cent for panels as large as 10 square feet in area.

If h is very large, which amounts to saying that the temperature gradient in the metal edge is the same as that in the insulating material far removed from the edge, equation (3) reduces to:

$$I=\frac{PKt}{Ak} \tag{4}$$

which could be written down directly from elementary principles, and represents the case in which the edge effect is greatest.

[2] The derivation of this equation is given in Appendix I.
[3] See Appendix I.

If no metal were present around the edges, the transmittance C of any panel would be:

$$C=\frac{Akh}{2ah+2k} \tag{5}$$

The transmittance T of any panel with complete metal inclosure is evidently equal to $C\,(1+I)$.

From (5) and (1),

$$T=\frac{Akh}{2ah+2k}\left[1+\frac{Pah}{Ak\left[\frac{ah+k}{Kt}+\gamma\sqrt{\frac{ah+k}{aKt}}\right]}\right] \tag{6}$$

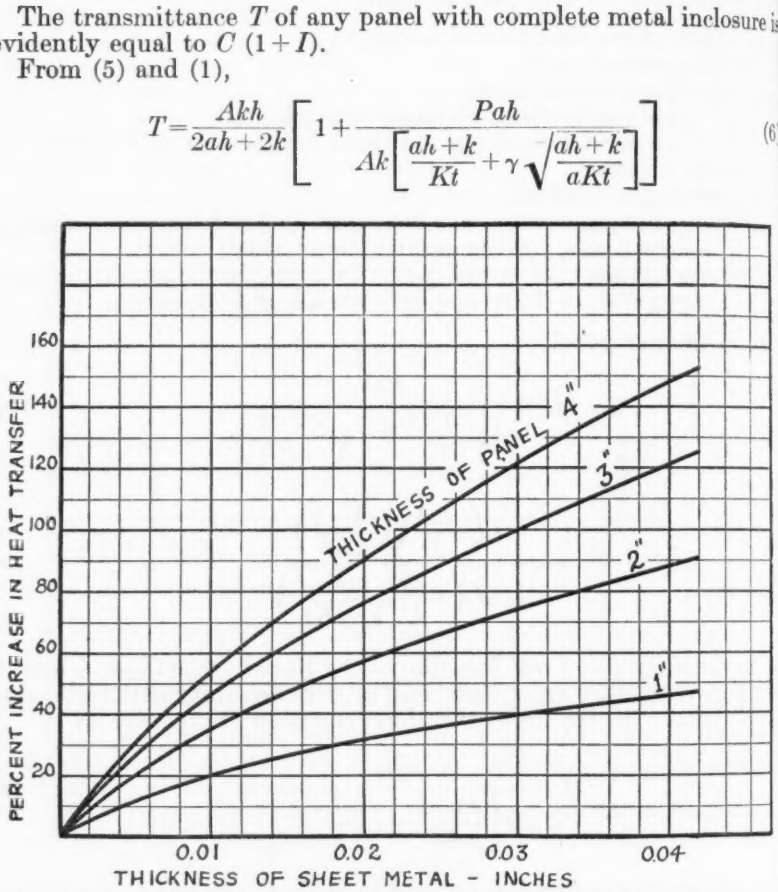


FIGURE 2.—*Per cent increase in heat transfer through 40 by 40 inch panel, due to complete steel inclosure*

Numerical calculations of practical cases show that the heat flow through the metal edges is not greatly affected even if the insulation is considered perfect. In such an event no assumption of linear heat flow through the insulating material is necessary, and it is therefore concluded that this assumption introduces no significant error in the calculation of heat flow in the metal. Numerical calculation also shows that the percentage decrease in heat transfer through the insulation due to the presence of the metal edges is small, and therefore the error involved in the assumption of linear heat flow through the insulation is practically insignificant.

Figure 2 shows the percentage increase (I, equation (1)) in heat transfer resulting from the use of a metal inclosure, plotted against the thickness of the metal (steel) used for the inclosure. A family of

urves is shown, each member applying to a particular thickness of nsulation. It will be noted that the percentage increase in heat ransfer increases with thickness of insulation. The absolute increase n heat transfer, however, decreases with increasing thickness of insu-ation, as must be evident from elementary principles. Figure 3 shows he absolute values of the resistance and transmittance, plotted gainst thickness of insulation. Each curve corresponds to a par-icular thickness of metal.

In the calculations the following data have been used:

k=0.002 B. t. u. hour^{-1} inch^{-1} (°F.)$^{-1}$ (average insulating material).
h=0.01 B. t. u. hour^{-1} inch^{-2} (°F.)$^{-1}$ (still air).
K=2 B. t. u. hour^{-1} inch^{-1} (°F.)$^{-1}$ (steel).
$\frac{P}{A}$=0.1 inch^{-1} (40 by 40 inch panel).

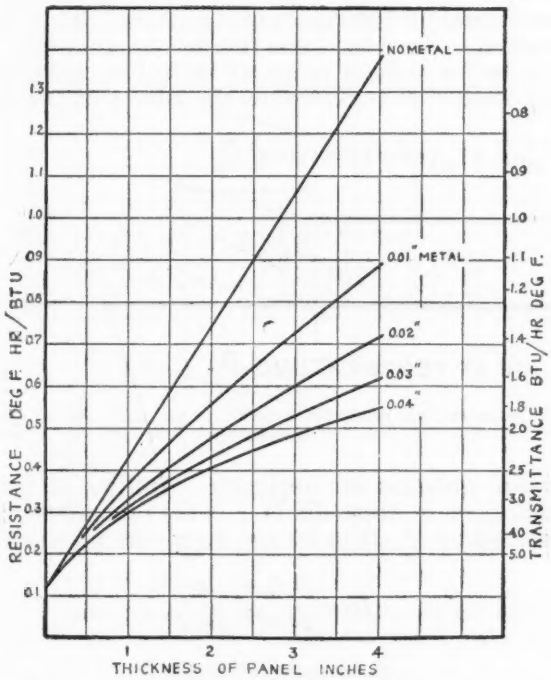


FIGURE 3.—*Transmittance and resistance of 40 by 40 inch panel, as affected by the thickness of panel and thickness of steel inclosure*

Since the percentage increase in heat transfer is nearly proportional o the value of $\frac{P}{A}$, values for panels of various sizes can readily be omputed by a simple multiplication. To avoid inconsistencies, a ingle unit of length (the inch) has been used throughout.[4] Round

[4] The familiar hybrid conductivity unit containing two units of length, the inch and the foot, is very inconvenient and illogical in dealing with heat flow in more than one direction. British units are used, since the majority of American engineers, to whom the paper is primarily addressed, are accustomed to think in terms of these units. The advantages of a decimal system are very great, but so many extraneous units; for example, the calorie, have been introduced into the various metric systems that the latter are almost as bad as the various British systems. The universal use of decimal multiples of c. g. s. units would be a great step forward.

numbers, closely approximating average experimental values, have been used for the thermal properties of the materials. For relatively small changes in the value of k (through the range of ordinary insulating materials) the percentage increase in heat transfer is approximately inversely proportional to k.[5] The effect of changes in the value of h can not be approximated so simply, and recourse must be made to the original equations. The value of the quantity γ varies little in the range of practical cases, and the average value of 1.05 is sufficiently close. In the calculations for Figure 2, γ varied from 1.03 to 1.07.

III. EFFECT OF A SMALL THERMAL SHORT CIRCUIT IN THE CENTRAL PORTION OF A PANEL

In Figure 4, R is a rod of radius r_2 in metallic thermal contact with the sheet metal on both sides of the panel. This thermal short circuit is assumed to have the same thermal conductivity as the sheet metal, and to be far enough removed (a foot or so) from the edge or from other similar rods such that the effects of the latter on the

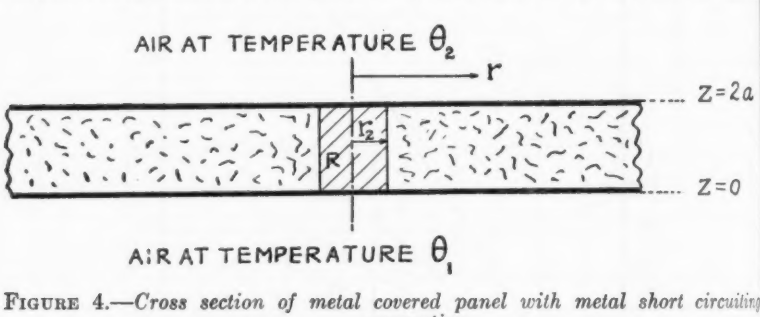


FIGURE 4.—*Cross section of metal covered panel with metal short circuiting connection*

particular rod in question are negligible. Outline of the solution of this problem is given in Appendix II. If the rate of heat flow through the rod is denoted by H_2, then for rod diameters up to about one-half inch,

$$H_2=\frac{\pi r_2^2 h(\theta_2-\theta_1)}{2at\alpha^2+\lambda\alpha r_2} \tag{8}$$

where

$$\lambda=2.3\alpha r_2 \log_{10}\frac{1.12}{\alpha r_2} \tag{9}$$

and

$$\alpha^2=\frac{ah+k}{aKt} \tag{10}$$

The effect of the presence of the metal connection on heat flow through the insulation is not significant, since the area of the insula-

[5] The approximation becomes less exact as the thickness of the insulation is decreased.

[6] Values of γ for values of the argument greater than 4 (always the case in a panel of practical dimensions) can readily be computed by means of the very good approximation

$$\gamma=\frac{J_0(iz)}{-iJ_1(iz)}=\sqrt{\frac{z}{z-1}} \tag{}$$

This equation can be deduced from the semiconvergent expressions for Bessel's functions.

on is very large compared with that of the disturbed region around e metal connection.

The rate of heat flow through a steel short circuit is plotted in gure 5. The figure is self-explanatory and need not be discussed any extent. By comparing the values with those in Figure 3, will be noticed that the transmittance of a short circuit of reasonable e is small compared to that of a 40 by 40 inch panel.

If the short-circuiting rod is not in metallic thermal contact with e metal surfaces, or if no metal surfaces are present, its effect is ctically insignificant on account of its relatively small area. A

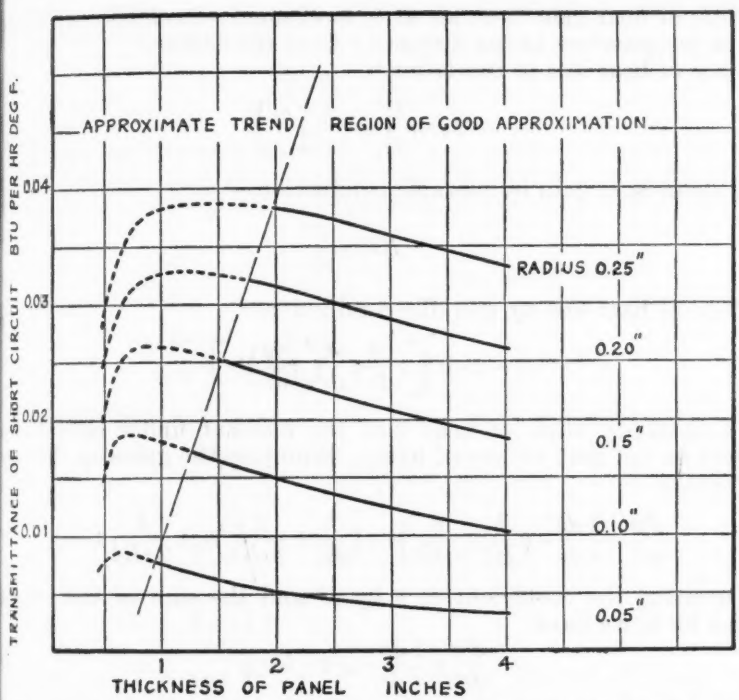


FIGURE 5.—*Effective transmittance of thermal short circuiting steel connection, as affected by thickness of panel and size of metal connection*

Sheet steel on surfaces 0.02 inch thick.

od example of this is a nail running completely through the insulaon. In such a case the heat flow is evidently given by

$$H_2 = \frac{\pi r_2^2(\theta_2 - \theta_1)h}{2} \tag{11}$$

e thermal resistance of the rod itself being negligible in comparison th the surface resistances on each end.[7]

[7] For a discussion of the effect of metallic members projecting part way into the insulating material, see H. Schofield, Phil. Mag., 7 series, 5, p. 567; 1928.

IV. APPENDIX I. METAL EDGES

Figure 1 shows a cross section of a circular panel surrounded the edges in such a way that no heat is lost or gained laterally. T general outline of the procedure and the assumptions used in t derivation of the equations has already been given and will not repeated here.

Consider the state of affairs in the metal on the warm side $z=2$ with particular reference to any ring element of infinitesimally sm width δr. It is evident from symmetry that the temperature uniform around the ring.

Rate of heat gain from air at θ_2 to element $=2\pi r\delta r h(\theta_2-\theta)$ where is the temperature at the distance r from the center.

Rate of heat loss to insulation =

$$2\pi r\delta r\frac{k}{a}\left[\theta-\frac{\theta_2+\theta_1}{2}\right]$$

Rate of heat gain by metallic conduction =

$$-Kt\,2\pi r\frac{d\theta}{dr}$$

Rate of heat loss by metallic conduction =

$$-2\pi Kt\left[r\frac{d\theta}{dr}+\frac{d}{dr}\left(r\frac{d\theta}{dr}\right)\delta r\right]$$

In a steady state of heat flow the element under considerati suffers no net gain or loss of heat. Equating the gains to the loss we obtain

$$\frac{d^2\theta}{dr^2}+\frac{1}{r}\frac{d\theta}{dr}-\left(\frac{h}{Kt}+\frac{k}{aKt}\right)\theta+\left(\frac{h}{Kt}+\frac{k}{2aKt}\right)\theta_2+\frac{k}{2aKt}\theta_1=0 \qquad (1)$$

Denoting the coefficient of θ by α^2 and the sum of the consta terms by b, we have

$$\frac{d^2\theta}{dr^2}+\frac{1}{r}\frac{d\theta}{dr}-\alpha^2\theta+b=0 \qquad (2)$$

This is a modified form of Bessel's equation of order zero, and particular solution is easily found to be

$$\theta=AJ_0(i\alpha r)+\frac{b}{\alpha^2} \qquad (3)$$

where A is an arbitrary constant, J_0 denotes the Bessel function zero order, and i is the usual symbol for $\sqrt{-1}$. The function J_0 a real function of the pure imaginary argument $i\alpha r$.

The complete solution of equation (2) will contain a Bessel's fu tion of the second kind which becomes infinite at the origin, and c not, therefore, appear in the solution of the present problem. If denotes the temperature (as yet unknown) of the edge $r=r_1$ a $z=2a$, then equation (3) becomes

$$\theta=\left(\theta_3-\frac{b}{\alpha^2}\right)\frac{J_0(i\alpha r)}{J_0(i\alpha r_1)}+\frac{b}{\alpha^2} \qquad (4)$$

On the cold surface $z=0$ a similar argument yields the equation

$$\theta=\left(\theta_4-\frac{c}{\alpha^2}\right)\frac{J_0(i\alpha r)}{J_0(i\alpha r_1)}+\frac{c}{\alpha^2} \tag{5}$$

here θ_4 is the temperature on the cold edge $r=r_1$ and $z=0$, and

$$c=\left(\frac{h}{Kt}+\frac{k}{2aKt}\right)\theta_1+\frac{k}{2aKt}\theta_2 \tag{6}$$

Since no heat is lost or gained by the metal along the edge, the mperature distribution in the metal at the edges must be linear ong the z axis. In terms of the unknown temperatures θ_3 and θ_4, is distribution is given by

$$\theta=\theta_4+\frac{\theta_3-\theta_4}{2a}z \tag{7}$$

The unknown temperatures θ_3 and θ_4 can be evaluated by con- dering the fact that there can be no discontinuity in temperature adient in the metal where it bends around the edges. We therefore n write

$$\left(\frac{\partial\theta}{\partial r}\right)_{r=r_1}=-\left(\frac{\partial\theta}{\partial z}\right)_{z=2a} \qquad \text{(on warm side)} \tag{8}$$

nd

$$\left(\frac{\partial\theta}{\partial r}\right)_{r=r_1}=\left(\frac{\partial\theta}{\partial z}\right)_{z=0} \qquad \text{(on cold side)} \tag{9}$$

Differentiating equations (4), (5), and (7), yields, respectively:

$$\left(\frac{\partial\theta}{\partial r}\right)_{r_1}=-\left(\theta_3-\frac{b}{\alpha^2}\right)\alpha\frac{iJ_1(i\alpha r_1)}{J_0(i\alpha r_1)} \tag{10}$$

$$\left(\frac{\partial\theta}{\partial r}\right)_{r_1}=-\left(\theta_4-\frac{c}{\alpha^2}\right)\alpha\frac{iJ_1(i\alpha r_1)}{J_0(i\alpha r_1)} \tag{11}$$

$$\left(\frac{\partial\theta}{\partial z}\right)=\frac{\theta_3-\theta_4}{2a} \tag{12}$$

The values of θ_3 and θ_4 can be obtained by the use of these equa- ons. Substituting their values in equations (4) and (5). and defin- g a quantity,

$$\gamma=\frac{J_0(i\alpha r_1)}{-iJ_1(i\alpha r_1)}$$

e have finally

$$\theta=\frac{b}{\alpha^2}-\frac{\gamma(b-c)}{2\alpha^2(\gamma+a\alpha)}\frac{J_0(i\alpha r)}{J_0(i\alpha r_1)} \qquad \text{(warm side)} \tag{13}$$

$$\theta=\frac{c}{\alpha^2}+\frac{\gamma(b-c)}{2\alpha^2(\gamma+a\alpha)}\frac{J_0(i\alpha r)}{J_0(i\alpha r_1)} \qquad \text{(cold side)} \tag{14}$$

The temperature difference $\Delta\theta$ between corresponding points at $=2a$ and $z=0$ on a cylinder of radius r is the difference between quations (13) and (14), or

$$\Delta\theta=\frac{b-c}{\alpha^2}-\frac{\gamma(b-c)}{\alpha^2(\gamma+a\alpha)}\frac{J_0(i\alpha r)}{J_0(i\alpha r_1)} \tag{15}$$

The rate of heat transfer through the insulation (on the origin assumption of linear flow) is given by

$$H_1 = \int_0^{r_1} 2\pi r \frac{k}{2a} \Delta\theta dr \tag{16}$$

Substituting equation (15) in equation (16) and integrating, yiel

$$H_1 = \frac{\pi k(b-c) r_1^2}{2a\alpha^2}\left[1 - \frac{2}{r_1\alpha(\gamma + a\alpha)}\right] \tag{17}$$

If no metal were present around the edges, a very elementary ca culation shows that the rate of heat transfer would be equal to t coefficient of the bracketed expression in equation (17). The decreas in heat flow through the insulation, due to the presence of the meta around the edges, is therefore given by

$$\frac{\pi k(b-c) r_1}{a\alpha^3(\gamma + a\alpha)} \tag{18}$$

The heat flow through the metal edge is evidently given by th expression:

$$\frac{2\pi r_1 Kt(\theta_3 - \theta_4)}{2a} \tag{19}$$

By the use of equations (13) and (14), this expression is easil evaluated and found to be:

$$\frac{\pi r_1 Kt(b-c)}{\alpha(\gamma + a\alpha)} \tag{20}$$

The net increase ΔH in total rate of heat flow through the panel, du to the presence of the metal edges, is the difference between equatio (20) and (18), or

$$\Delta H = \frac{\pi r_1 (b-c)}{\alpha(\gamma + a\alpha)}\left[Kt - \frac{k}{a\alpha^2}\right] \tag{21}$$

Were there no metal present around the edges, the total rate of hea transfer H through the panel would be

$$H = \frac{\pi r_1^2 hk(\theta_2 - \theta_1)}{2(ah + k)} \tag{22}$$

The percentage increase in heat transfer, due to the presence of th metal edges, is equal to $\frac{\Delta H}{H}$. Substituting the values of b, c, and α, we have finally,

$$\frac{\Delta H}{H} = \frac{2ah}{kr_1\left(\frac{ah+k}{Kt} + \gamma\sqrt{\frac{ah+k}{aKt}}\right)} \tag{23}$$

This is identical with equation (1) in the text, since $\frac{2}{r_1} = \frac{P}{A}$.

A similar analysis applied to an infinite straightedge (therefore suming at the outset that the heat flow in the metal edge is directly oportional to the length of the edge and independent of the area of e panel) involves the use of exponential functions and yields uation (23) in the special limiting case where $\gamma \to 1$. Evidently is must necessarily follow, and amounts to nothing more than a eck on the analysis.

V. APPENDIX II, THERMAL SHORT CIRCUIT

Referring to Figure 4, the differential equation of heat flow in the etal surfaces in the range $r > r_2$ is evidently the same as in the previ- s case. The particular solution required, however, is different, ce the boundary conditions are different. We are no longer con- rned with the value of θ when $r = 0$, but when the value of r becomes rge, θ must approach the value it would assume were there no metal ort circuits. The general solution of equation (2), Appendix I is

$$\theta = A' J_0(i\alpha r) + B' Y_0(i\alpha r) + \frac{b}{\alpha^2} \tag{1}$$

By choosing certain values of the arbitrary constants A' and B', e can write

$$\theta = A\left\{\left[\log \frac{2i}{\beta}\right][J(i\alpha r)] - Y_0(i\alpha r)\right\} + \frac{b}{\alpha^2} \tag{2}$$

The quantity in the braces is real, vanishes for infinite values of and is therefore the solution required, since $\frac{b}{\alpha^2}$ is the temperature of e metal surface were there no metal short circuits present.

Y is the more common notation for Bessel's functions of the second nd, although many other notations are used. β is a fixed numerical nstant having the value 1.7811. The bracketed expression in uation (2) is a real function of r and was denoted by Hankel[9] as

$$\frac{i\pi}{2} H_0(i\alpha r)$$

hen $$r = r_2 \text{ and } z = 2a,\ \theta = \theta_3.$$

iminating the constant A from equation (2) by this means yields

$$\theta = \frac{b}{\alpha^2} + \left(\theta_3 - \frac{b}{\alpha^2}\right)\frac{H_0(i\alpha r)}{H_0(i\alpha r_2)} \tag{3}$$

lid in the range $r > r_2$ and $2a - t < z < 2a$.

Within the cylindrical rod short circuiting the two thin metal sur- ces, we must satisfy the equation $\nabla^2\theta = 0$ with the following bound- y conditions: When

$$z = a,\ \theta = \frac{\theta_2 + \theta_1}{2}$$

[9] See Jahnke-Emde "Funktionentafeln mit Formeln und Kurven," Teubner, p. 94; 1909.
Hankel, Mathematische Annalen, **1**, p. 483; 1869; **8**, p. 453; 1875.

$z=2a, \dfrac{\partial\theta}{\partial z}=0$ (neglecting the very small amount of heat receiv directly from the warm air over the relative small area πr_2^2).

$$\left.\begin{matrix}2a-t<z<2a\\ r=r_2\end{matrix}\right\}, \frac{\partial\theta}{\partial r}=\left(\frac{d\theta}{dr}\right)_{r=r_2} \text{ from equation (3)}$$

$$\left.\begin{matrix}a<z<2a-t\\ r=r_2\end{matrix}\right\}, \frac{\partial\theta}{\partial r}=0$$

The solution satisfying these conditions, valid in the range $r<$ and $a<z<2a$, can be found without great difficulty, and is as follow

$$\theta=\frac{\theta_2+\theta_1}{2}-\frac{8a\alpha\left(\frac{b}{\alpha^2}-\theta_3\right)}{\lambda\pi^2}\sum_{n=1}^{n=\infty}\frac{\sin\frac{(2n-1)\pi}{2}\sin\frac{(2n-1)\pi t}{2a}}{(2n-1)^2 iJ_1\left(i\frac{(2n-1)\pi r_2}{2a}\right)}$$

$$\sin\frac{(2n-1)\pi(z-a)}{2a}J_0\left(i\frac{(2n-1)\pi r}{2a}\right)$$

where

$$\lambda=\frac{H_0(i\alpha r_2)}{iH_1(i\alpha r_2)}$$

At the boundary region $r=r_2$ and $2a-t<z<2a$, equations (3) a (4) should give identical values of temperature (θ_3) as well as norm derivative, in order to satisfy the physical demand of continuity temperature. Evidently they will not do this exactly, but the di crepancy is negligible, since over the small distance from $z=2a-t$ $z=2a$, the temperature given by equation (4) is very nearly constan The elimination of θ_3 by using equations (3) and (4) is therefo accurate enough for the present purpose.

When $r=r_2$ and $z=2a$

$$\theta=\theta_3=\frac{\theta_2+\theta_1}{2}-\frac{8a\alpha\left(\frac{b}{\alpha^2}-\theta_3\right)}{\lambda\pi^2}\sum_{n=1}^{n=\infty}\frac{\sin\frac{(2n-1)\pi t}{2a}}{(2n-1)^2}\frac{J_0\left(i\frac{(2n-1)\pi r_2}{2a}\right)}{iJ_1\left(i\frac{(2n-1)\pi r_2}{2a}\right)}$$

Solving for θ_3

$$\theta_3=\frac{\frac{8ab}{\pi^2\alpha\lambda}\sum+\frac{\theta_2+\theta_1}{2}}{1+\frac{8a\alpha}{\pi^2\lambda}\sum}$$

The rate of heat flow, H_2, down the metal rod is evidently equal

$$2\pi r_2 Kt\frac{d\theta}{dr} \quad \text{(from equation (3))}$$

therefore,

$$H_2=\frac{2\pi r_2 Kt\alpha}{\lambda}\left(\frac{b}{\alpha^2}-\theta_3\right)$$

bstituting the value of θ_3, we have

$$H_2=\frac{2\pi r_2 Kt\alpha}{\lambda}\left[\frac{b}{\alpha^2}\cdot\frac{\frac{\theta_2+\theta_1}{2}+\frac{8ab}{\pi^2\alpha\lambda}\sum}{1+\frac{8a\alpha}{\pi^2\lambda}\sum}\right] \tag{8}$$

The series, denoted by the abbreviation Σ, is approximately equal, r small values of r_2 less than about 0.25 inch, to the expression

$$\sum=\frac{\pi^2 t}{4r_2}$$

This equation is obtained by considering the limiting forms of pression of the quantities involved as r_2 approaches zero. The nitations of the approximation can be shown only by numerical lculation. The approximate value of λ (equation (9) in text) is least as accurate as the approximation for Σ, and was obtained by e same method.

Using this approximation, and substituting the value of the quan- y b, we have finally, after considerable algebra,

$$H_2=\frac{\pi r_2^2 h(\theta_2-\theta_1)}{2at\alpha^2+r_2\alpha\lambda} \tag{9}$$

This expression can be obtained directly by assuming at the outset at each end of the metal short-circuiting post has an infinitely nducting surface layer of small thickness t.

WASHINGTON, April 30, 1930.

EFFECTS OF GASES ON PHOTOIONIZATION OF CÆSIUM BY LINE ABSORPTION

By F. L. Mohler and C. Boeckner

ABSTRACT

Relative measurements of the photoionization by line absorption in cæsium apor with and without foreign gases were made by the space-charge method. the effect of a collision with a gas molecule is to change the probability of nization from E_o to E_f, then the probability E_p at a gas pressure p is given by

$$\frac{E_o}{E_o - E_p} = \frac{E_o}{E_o - E_f}\left(1 + \frac{1}{A\sigma^2\tau' p}\right)$$

here A is a known constant, σ is the distance between atom centers at collision d τ' is the life of the excited state.

Nitrogen reduces the ionization of states 4 P to 8 P by about the same amounts. τ' is of the order of 10^{-21} cm² sec. and $E_f/E_o = 0.1$. Hydrogen gives about e same result. Helium increases the ionization of 4 P (E_f/E_o for 4 P_1 is 3) and creases the effect of other lines to 60 or 70 per cent at high pressure. $\sigma^2\tau'$ is $^{-21}$ for 5 P and less for other states. Argon gives very little effect. The fectiveness of nitrogen increases about threefold when the cæsium pressure is anged from 0.012 to 0.002 mm, and the computed change in τ' accounts for is variation. Results indicate a value of σ between 1.4 and 4×10^{-8} for all reign gases, while the value for the Cs-Cs collision giving ionization was ten nes this.

CONTENTS

	Page
I. Theory	399
II. Procedure	401
II. Experimental results	402
1. Nitrogen	402
2. Helium	404
3. Hydrogen	405
4. Argon	406
5. Effect of nitrogen as a function of cæsium pressure	406
V. Discussion	406

I. THEORY

Another paper by the authors [1] describes experiments on the photo-ectric ionization of cæsium vapor by radiation of wave length nger than the absorption series limit. The results indicate that is ionization involves the production of an excited atom by line sorption and the subsequent collision of the excited atom and a rmal atom. This supports a theory suggested by Franck that nization results from the combination of an excited atom and a rmal atom to form a molecule ion.

This paper reports experiments on the modifications of this ioniza-on which are produced when foreign gases are added to the cæsium. he results can be understood without any assumptions as to the

[1] Mohler and Boeckner, B. S. Jour. Research, 5 (RP186), p. 51; July, 1930.

mechanism of the ionization process except that excited atoms colli with normal cæsium atoms and are ionized with a probability whi depends on the state of excitation. The collisions with other ato will change the state of excitation and modify the probability ionization.

The ionization process is itself a collision process, and a bri recapitulation of the theory and results presented in the first pap will be given here. Experimental data were reduced to values the probability E of ionization of the different excited states expres as a function of the cæsium pressure. The probability of a collisi during the lifetime of an excited state [2] is

$$P=\frac{\tau}{T+\tau} \tag{1}$$

where T is the mean time between collisions and τ the mean life the excited state. For the general case of two gases of molecul weights m_1 and m_2

$$T=\frac{1}{A\,\sigma^2 p},\quad A=2.0\times 10^{22}\sqrt{\frac{m_1+m_2}{m_1\,m_2}},$$

$$\frac{1}{P}=1+\frac{1}{A\,\sigma^2\,\tau\,p} \tag{2}$$

where p is the pressure in millimeters of mercury and σ is the distan of approach of the two atoms at collision. The constant is evaluate for a working temperature of 500° K.

We assume that the probability of ionization E at a pressure p equal to the probability of ionization at a collision, E_c, times th probability of a collision during the life of the excited state

$$E=E_c\,P$$

$$\frac{1}{E}=\frac{1}{E_c}\left(1+\frac{1}{A\,\sigma^2\,\tau\,p}\right) \tag{3}$$

Plots of reciprocals of E and p gave straight lines and Table 1 re peats the numerical values of E_c and $\sigma^2\tau$ derived from these line Collisions with cæsium atoms modify the lives of the excited state If we assume that each collision destroys the excited state, then th actual life τ' is given by

$$\frac{1}{\tau'}=\frac{1}{\tau}+\frac{1}{T} \tag{4}$$

At the pressure for which $E=\frac{1}{2}E_c$, $\tau=T$ and $\tau'=\frac{1}{2}T$.

For states 5 P to 8 P the half value is reached at nearly the sam pressure 0.0038 mm, and from this one can compute the ratio of τ' to τ for any cæsium pressure.

$$\frac{\tau}{\tau'}=1+\frac{p}{0.0038} \tag{5}$$

[2] Turner, Phys. Rev., 23, p. 464; 1924.

TABLE 1.—*Constants for cæsium-cæsium collisions* [1]

m	1S−mP	E_c	$\sigma^2\tau$	p in mm for $E/E_c = ½$
4	3,888	0.003	0.22×10^{-19}	0.02
5	3,612	.154	1.0×10^{-19}	.0042
6	3,477	.26	1.1×10^{-19}	.0032
7	3,398	.40	1.1×10^{-19}	.0042
8	3,347	.50	1.0×10^{-19}	.0038
9, 10	3,300	.77	1.2×10^{-19}	.0032
12, 13	3,250	.89	3.3×10^{-19}	.0011
16	3,225	.93	16×10^{-19}	.0002
25	3,200	1.0	48×10^{-19}	.00007

[1] Mohler and Boeckner, B. S. Jour. Research, **5** (RP186); July, 1930.

The collision of an excited atom with a foreign gas will change the probability of ionization, and the simplest case is when the collision reduces the probability to zero. Then, if E_o is the probability of ionization in pure cæsium vapor at a fixed vapor pressure and E_p the probability of ionization with a foreign gas at a partial pressure, p, the probability of collision of an excited atom with the foreign gas is

$$P=\frac{E_o-E_p}{E_o}$$

More generally the collision will change the probability of ionization from E_o to E_f and

$$P=\frac{E_o-E_p}{E_o-E_f}=\frac{E_o-E_p}{E_o}\frac{E_o}{E_o-E_f}$$

Equation (2) becomes

$$\frac{E_o}{E_o-E_p}=\frac{E_o}{E_o-E_f}\left(1+\frac{1}{A\sigma^2\tau' p}\right) \tag{6}$$

II. PROCEDURE

We use as before the neutralizing effect of positive ions on a thermionic current limited by negative space charge to measure the photoionization. Curves of photoionization as a function of wave length are obtained in pure cæsium and in cæsium with a foreign gas. The gas reduces the amplification factor of the space-charge tube by an unknown amount, but we can safely assume that the presence of gas does not change the number of ions produced by direct ionization by wave lengths shorter than the series limit (3,184). If the two curves are reduced to the same scale of ordinates at and beyond the limit, then the ratio of ordinates at any wave length in the region of line absorption measures the effect of the foreign gas in the process of ionization. If the line absorption is not changed by the gas, this ratio of ordinates is E_p/E_o, the ratio of probabilities of ionization of an excited atom with and without the gas present. Absorption lines are broadened by foreign gas, but by an amount that can be neglected for the low pressures here used.[3]

[3] Füchtbauer and Hoffman, Ann. der Phys., **43**, p. 96, 1914, give the broadening of cæsium lines by nitrogen as 0.3 A at 2,360 mm, or 0.00013 A per mm.

To improve precision we have used a refinement of the space-cha method developed by Lawrence and Edlefsen[4] in most of this wo Instead of balancing the dark current in a 2-electrode tube, they two cylindrical anodes around a single axial cathode. Light admitted to one chamber and the resulting difference in current the two anodes is measured. This automatically compensates small fluctuations. We have followed the general scheme of t design and electrical circuits described by Lawrence and Edlef except that illumination was through a slit in the side of one cylind

The tubing connecting the ionization chamber to the pumps h a 2 cm section of 1 mm capillary tubing at about 15 cm from t chamber, and the cæsium was kept on the chamber side of the ca lary and maintained by a separate heater at the temperature wh determined the vapor pressure. Liquid cæsium quickly collected the constriction and sealed it, preventing rapid loss into the pu system. Application of a flame opened the chamber to the rest of t system whenever it was desired. A mercury cut-off on the pu side of a liquid air trap and McLeod gauge served to admit and m the gas.

Light from a Mazda projection lamp, resolved by a Bausch Lomb monochromator, was used for continuous spectrum illumin nation. Studies of the effect of the 3,888 helium line were made direct comparison with the effect of the 3,130 mercury line. mercury arc and a helium tube were arranged so that both illumina the slit of the monochromator, and the comparison was made changing the monochromator setting. In this case the space cha effect is very large and not proportional to the intensity; so, for ea condition, the current intensity relation had to be determined. T helium line is coincident with $1\ S-4\ P_1$ and gives excited atoms the state $4\ P_1$. The continuous spectrum peak is the unresol effect of 3,888 and 3,877 giving states $4\ P_1$ and $4\ P_2$, and the latte probably predominant because it is more strongly absorbed.

It is to be expected that the effects of different gases are qu sensitive to impurities, but it is not feasible to obtain high purity the usual technique of prolonged streaming or flushing out of t system without accumulating impurities in the cæsium. This probably the chief source of experimental uncertainty.

III. EXPERIMENTAL RESULTS

1. NITROGEN

Figure 1 shows curves of photoionization versus wave length pure cæsium at 0.005 mm, and in cæsium vapor with 0.143 mm nitrogen and with 2.25 mm. The effect is to reduce ionization line absorption at all lines on the red side of 3,200 A, and all resolv lines are reduced by about the same magnitude. The sensitivity the space charge effect becomes very low for pressures greater than or 3 mm of nitrogen. Experiments on the ionization produced by t 3,888 helium line gave results which were about the same as th obtained by continuous spectrum excitation; showing that the sta $4\ P_1$ and $4\ P_2$ are modified by nitrogen in much the same way.

[4] Lawrence and Edlefsen, Phys. Rev., 34 p. 233; 1929.

From the ratio of ordinates, E_p/E_o, we derive $E_o/(E_o-E_p)$ and gure 2 gives a plot of this function against $1/p$. Results are not curate enough to prove that a linear relation exists, but straight s fall well within the range of experimental error and permit an erpretation of results in terms of equation (6). From this equation see that if the probability of ionization is reduced to zero at a lision the intercept at $1/p=0$ will be one. The intercept for the olved lines, 3,349 to 3,888, is nearly one but definitely above, both

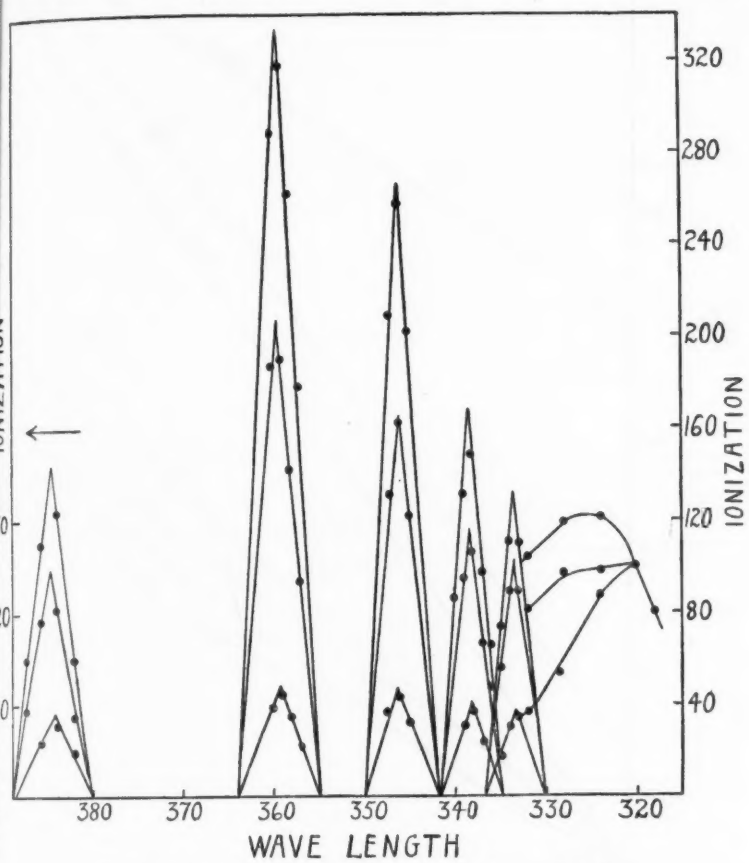


FIGURE 1.—*Ion current as a funtion of wave length*

The upper curve gives the effect in pure caesium, the middle curve with nitrogen at 0.143 mm, the lower curve with nitrogen at 2.25 mm.

Figure 2 and in other similar runs. For settings near the limit, tably at 3,240, incomplete resolution may partially mask the pres- re variation and the observed difference between 3,240 and other ve lengths is in the direction to be expected from this cause. Of urse, in reciprocal plots the error becomes very great for large dinates. The lines in Figure 2, unlike the reciprocal plots for ization as a function of pressure, do not change progressively as e go to the higher states.

2. HELIUM

The effect of helium on photoionization is quite different from t of nitrogen. As it has a smaller effect on the space-charge effe wider pressure range could be studied. Figure 3 gives the relat

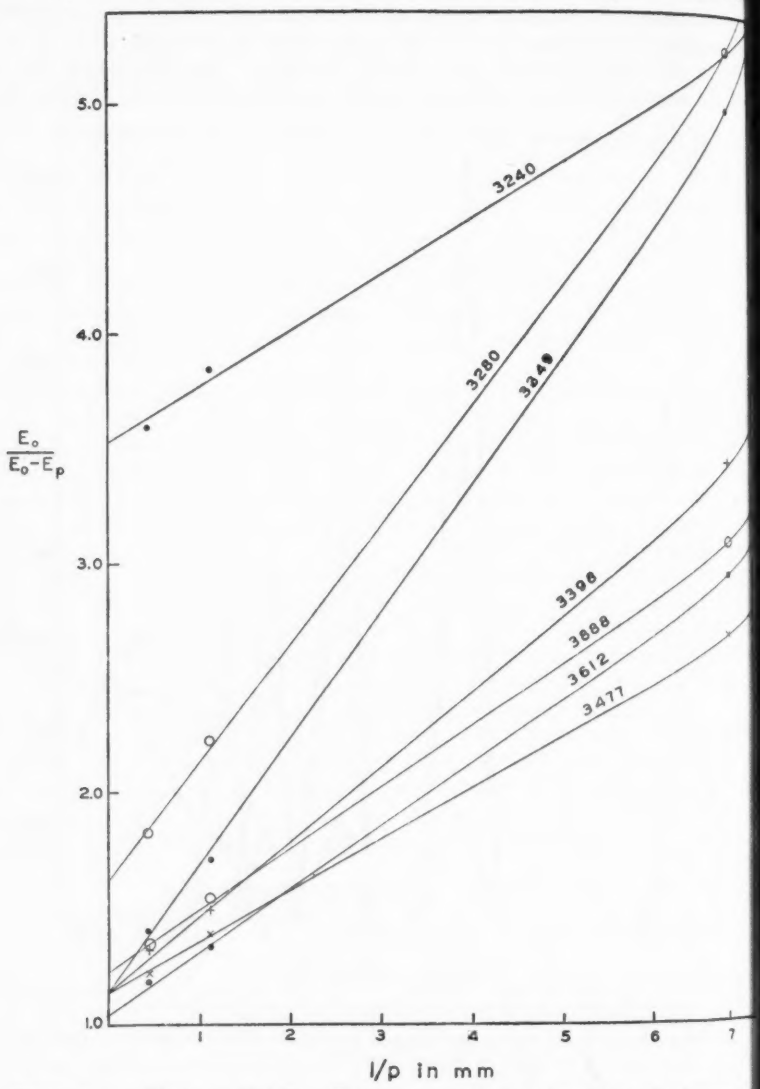


FIGURE 2.—*Plots of $E_o/(E_o-E_p)$ versus $1/p$ for the effect of nitrogen o cæsium ionization*

change in ionization, E_p/E_o, as a function of pressure. The ioni tion of states 4 P_1 and of 4 P_1 and 4 P_2 increases with the addition helium and the increase is different for the two cases. The ionizat of all other states is decreased somewhat, and apparently the pr ability has a minimum value at 2 or 3 mm and slowly increases higher pressure.

Plots $E_o/(E_o - E_p)$ against $1/p$ are shown in Figure 4. The measurements at lower pressures give a basis for drawing the straight lines, but the observed increase at high pressures gives, of course, a large departure from the linear relation near $1/p = 0$.

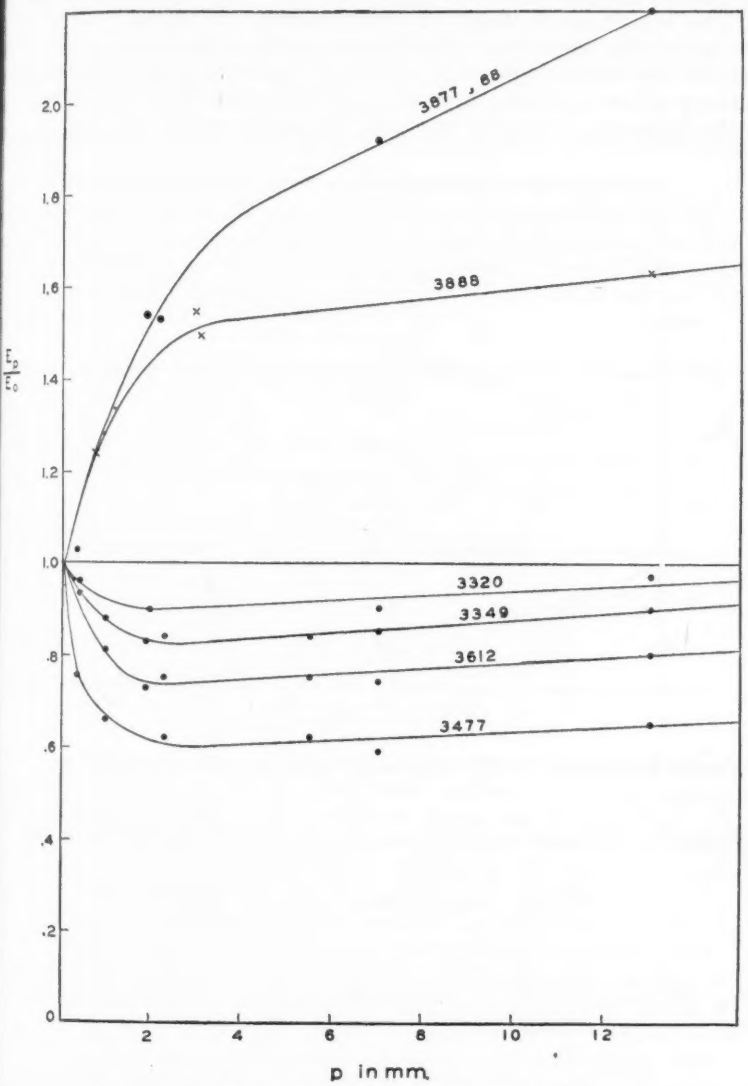


FIGURE 3.—*E_p/E_o as a function of pressure of helium*

3. HYDROGEN

Measurements with hydrogen are subject to experimental uncertainty because of reaction with the cæsium. After admission of hydrogen the pressure continuously drops, and prolonged pumping was required to again attain a vacuum. After several days of pump-

ing the tube was sealed off and the pressure again rose sufficiently t reduce sensitivity to line absorption to about 12 per cent of th vacuum value. The hydrogen must modify the cæsium parti pressure, but our method eliminates first-order errors from this caus Small hydrogen pressures give a marked decrease in the ionizatio and Table 2 gives results. A plot of $E_o/(E_o-E_p)$ against $1/p$ indicat that the best lines through observed points for states 5 P and 6 have intercepts near one. For higher states data for measured pre sures do not fall on lines through 1 at $1/p=0$ but the observed lo efficiency at an unknown high pressure indicates that for these stat too the intercept is nearly one and the other points are probably i error.

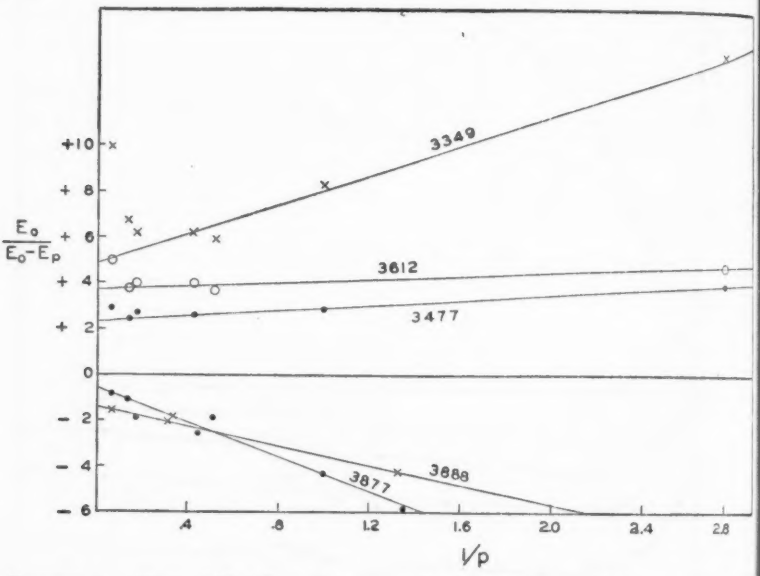


FIGURE 4.—*Plots of $E_o/(E_o-E_p)$ versus $1/p$ for the effect of helium on cæsium ionization*

TABLE 2.—*Ionization with hydrogen as compared with pure cæsium, E_p/E_o*

Line	0.02 mm	0.08 mm	0.15 mm	Unknown high pressure
3,877	0.77	0.59	----	----
3,612	.78	.52	0.36	0.12
3,477	.78	.52	.31	.14
3,398	.77	.68	.50	.12
3,347	.80	.78	.48	.15

Hydrogen is the most common impurity in alkali vapors, and th results show that it can be a serious source of error in any experimen involving the duration of excited states. These experiments were, i fact, initiated by the observation that hastily prepared ionizatio tubes gave an abnormally low sensitivity to line absorption. Carefull outgassed tubes seem to retain the full sensitivity, however, afte sealing off.

4. ARGON

Argon gives a large reduction in space-charge effect and a small change in relative sensitivity. Successive runs showed discrepancies which suggest that impurities play an important part. The effect on 3,877 and 3,888 was increased roughly 20 per cent by the addition of argon. The peaks at 3,612 and 3,477 were reduced to about 60 per cent by 2.6 mm of argon and other lines less. Reciprocal plots of data for this and lower pressures indicate that the lines for states above 4 P have intercepts near 1 at $1/p=0$.

5. EFFECT OF NITROGEN AS A FUNCTION OF CÆSIUM PRESSURE

The above results apply to the effects of a foreign gas at a fixed cæsium pressure of 0.005 mm. A series of measurements on the effect of 0.134 mm of nitrogen at various cæsium pressures is given in Table 3. The results show a marked increase in the effectiveness of nitrogen with decreasing cæsium pressure though accidental variations are rather large.

TABLE 3.—*Effect of 0.134 mm of nitrogen at various cæsium pressures in terms of* E_p/E_o

Line	Cæsium pressures			
	0.0019	0.0028	0.0048	0.0126
3,877	----------	0.74	0.68	0.89
3,612	0.46	.48	.66	.68
3,477	.42	.52	.63	.73
3,398	.52	.50	.71	.79
3,349	.61	.62	.80	.85
3,320	.67	.60	----------	.87
3,280	.60	.68	.81	.95

IV. DISCUSSION

Other studies of the various effects produced when excited atoms collide with other atoms or molecules [5] indicate that in some cases the predominant effect is a transition from the excited state to the normal state; in other cases the most probable result is a change in the state of excitation involving a minimum dissipation of energy. Boeckner [6] has studied resonance radiation of cæsium excited by the 3,888 helium line in pure cæsium and in the presence of helium. In pure cæsium only those lines are emitted which result from permitted radiation transitions from 4 P_1. Helium collisions change the state of excitation to the neighboring states 4 P_2 and 5 D, which differ from 4 P_1 by 0.01 and 0.04 volt, respectively. Transitions by collision to other states which all differ from 4 P_1 by more than 0.14 volt are quite negligible. The effect of helium was to increase the ionization produced by 3,888. We know that in pure cæsium 4 P_2 is ionized with roughly the same probability as 4 P_1, so we conclude that the transitions to 5 D account for the change and that 5 D is much more readily ionized than the 4 P states.

[5] Ruark and Urey, Atoms, Molecules, and Quanta; McGraw Hill Co.
[6] Boeckner, B. S. Jour. Research, **5** (RP184), p. 13; July, 1930.

For all other cases we have no direct evidence as to the transitions involved. It seems reasonable to assume that other excited states are also changed to neighboring states by helium collisions. Since collisions with hydrogen and nitrogen reduce the probability to nearly zero, we conclude that most collisions in these gases give a nearly complete dissipation of energy. It is interesting to note that experiments on collision effects with excited mercury in the 2 $^3P_1$ state show that hydrogen and oxygen reduce the atom to the normal state, while for nitrogen, as well as for the noble gases, the predominant effect is the minimum energy change from 2 $^3P_1$ to 2 $^3P_0$.

Numerical values of $\sigma^2\tau'$ and of E_f/E_o are given in Table 4 for every case where experimental data justified a numerical estimate. They are computed from the slopes and intercepts of the straight lines given by reciprocal plots in accordance with equations (2) and (6). We include for comparison values of $\sigma^2\tau$ for cæsium-cæsium collisions. $\sigma^2\tau'$ for 5 P and 6 P remains of the same magnitude for all foreign gases except for the questionable value of argon. The observed differences in effectiveness at the same pressure are accounted for by the change in A in equation (6). These values are all of the order of 1 per cent of $\sigma^2\tau$ for cæsium-cæsium collisions. In the earlier paper we have estimated that for 5 P, τ is less than 10^{-6} and more than 10^{-6} which leads to a value of the collision radius between 10^{-7} and 3×10^{-7} for cæsium-cæsium collisions. For foreign gases, τ' is roughly $\frac{1}{2}$ τ and σ between 1.4 and 4×10^{-8} for 5 P. The radius for collisions with foreign gases agrees in magnitude with ordinary atomic dimensions; the radius for cæsium-cæsium collisions is abnormal. The results show that the large radii are not determined by the electron charge distribution in states of high quantum number, for they are not characteristic of the state of excitation.

TABLE 4.—*Constants for collisions of excited cæsium with gases*

Line	Cs-Cs	Cs-N_2		Cs-He		Cs-H_2		Cs-A	
	$\sigma^2\tau$	$\sigma^2\tau'$	E_f/E_o	$\sigma^2\tau'$	E_f/E_o	$\sigma^2\tau'$	E_f/E_o	$\sigma^2\tau'$	E_f/E_o
3888	0.22×10^{-19}	1.10×10^{-21}	0.18	0.067×10^{-21}	1.7	1.0×10^{-21}	0	----------	>
3877				.013	3.0				
3612	1.0	.93	.04	1.07	.74	1.0	0	0.07×10^{-21}	
3477	1.1	1.25	.12	.38	.56	1.0	0	$.07\times10^{-21}$	
3398	1.1	.83	.12	.50	.69	.45	0	$.04\times10^{-21}$	
3349	1.0	.51	.12	.16	.80	.25	0	----------	
3280	2.0	.76	.38	----------	----------	----------	----------	----------	
3240	6.0	3.5	.72	----------	----------	----------	----------	----------	

Table 5 gives values of $\sigma^2\tau'$ for nitrogen at various cæsium pressures based on a single observed point at 0.134 mm of nitrogen and a value of the intercept taken from Figure 2. The change in $\sigma^2\tau'$ according to the simple theory given in the introduction depends on the change in τ' with vapor pressure, for σ should remain constant. We include in Table 5 computed values based on the variation of τ' as given by equation (5). There is a qualitative agreement, though the accidental variations are large.

TABLE 5.—*Effect of nitrogen at various cæsium pressures*

Cs pressure	Theoretical change	$\sigma^2\tau' \times 10^{21}$				
		3,612	3,477	3,308	3,349	3,280
0.0126	1.0	0.89	0.76	0.57	0.37	0.16
.0048	1.9	.93	1.25	.83	.51	.76
.0028	2.5	2.1	2.2	2.4	1.4	1.9
.0019	2.9	2.3	3.5	2.2	1.5	3.3

This rough agreement is of some significance in connection with collision processes in pure cæsium vapor. The derivation of the variation in actual life resulting from collisions with cæsium atoms rests on the assumption that in a collision the excited state is destroyed whether or not ionization is produced. This assumption was introduced largely for simplicity. If excited states are destroyed only in the event of ionization, then the actual life will be modified much less than is predicted by equation (5). Observed variations are, if anything, greater than the predicted change. Support for the conclusion that excited states are destroyed at collision is found in the observation by Boeckner that the resonance radiation excited by 3,888 becomes very faint when the cæsium pressure is increased above a few thousandths and surface resonance was not observed at higher pressures.

In the earlier paper we give a picture of the ionization process which implies that some, if not all, of the collisions that fail to give ionization give band emission spectra. It will be of interest to look for a molecular emission spectrum excited by atomic absorption under conditions of moderately high pressure.

At the highest pressure given in Table 5 (0.012 mm) the value of τ' is about one-fifth of the radiation life for states 5 P to 8 P; and, to a first approximation, we can neglect τ in the relation $\frac{1}{\tau'}=\frac{1}{\tau}+\frac{1}{T}$ and assume that $\tau'=T$. Since T is proportional to $1/\sigma^2$ for cæsium-cæsium collisions, $\tau'\sigma^2$ (nitrogen) is proportional to the ratio of σ^2 for nitrogen to σ^2 for cæsium. The decrease in $\sigma^2\tau'$ as we go to higher states indicates a decrease in the ratio of collision areas for the two kinds of collisions. The collision areas for cæsium-cæsium collisions presumably decrease with increasing quantum number between 5 P and 10 P and the collision areas for cæsium-nitrogen collisions decrease much faster.

The magnitude of the collision area might be expected to depend on whether or not chemical combination can take place. At least this is indicated in experiments by Lunn and Bichowsky [7] on the scattering of atomic hydrogen by foreign gases. The excited cæsium-cæsium collision involves a chemical reaction according to our viewpoint, and the large collision area is to be expected.

We might expect that the nearly complete quenching given by both H_2 and N_2 results from a transfer of the excitation energy of the cæsium atom into vibration energy of the molecules. All the m P levels fall in the range of discrete vibration states for both molecules. This suggests that, where the energy difference between an excited

[7] Preliminary note, Phys. Rev., **35**, p. 563; 1930.

state and a vibrational level happens to be small, the value of σ wi be abnormally large. There is no evidence of any such effect and bot gases give values of σ much like helium.

The theory, as presented in the introduction and in the earlier pape gives an ideally simplified picture of the complicated processes tha are to be expected when an atom in a state of high quantum numbe collides with another atom. There are many possible transitions, an each will have a characteristic collision radius and efficiency. Th observed effect is presumably a sort of average of these differen primary effects. Again, there are many secondary effects, such a reabsorption of resonance radiation and successive collisions eithe reversing or increasing the effect of the first collision. These will, i general, give a curvature to the reciprocal plots and the procedure o drawing a straight line through observed points, which are to inaccurate to show a curvature, may involve a large systemati error. Detailed analyses of the results on quenching of resonanc radiation in mercury vapor have shown that these secondary effec are by no means negligible.[8] [9]

The important feature of this work is that for the first time it ha been possible to obtain approximate values of $\sigma^2\tau$ for a series o excited states in various gases with some qualitative evidence as t the effects produced at collision.

WASHINGTON, April 15, 1930.

[8] Foote, Phys. Rev., **30**, p. 288; 1927.
[9] Gaviola, Phys. Rev., **33**, p. 309; 1929.

A CALORIMETRIC DETERMINATION OF THERMAL PROPERTIES OF SATURATED WATER AND STEAM FROM 0° TO 270° C.

By N. S. Osborne, H. F. Stimson, and E. F. Fiock

ABSTRACT

A description is given of the method, apparatus, measurements, results, and formulations involved in the work on steam which has been completed to date at the National Bureau of Standards.

The method has been developed in accordance with the principles set forth in a rigorous analysis of the thermodynamic processes involved in a change in state of a saturated fluid.

The apparatus has been designed and built to provide a means for accurately controlling, observing, and accounting for the amount, the change in state, and the change in energy of a sample of water.

The observations have been carried out as a systematic series of experiments in the range from 0° to 270° C. (to 55 atmospheres pressure), yielding as a result the values of three characteristic thermal properties of the saturated fluid.

The formulation of the results establishes the values of heat content, latent heat, and entropy and constitutes an exhibit of the thermal behavior of saturated steam in the region covered by the experiments.

The results are assembled in a coherent, consistent table of the properties of steam, available as a foundation for a more complete steam table.

It is found that when reduced to a uniform basis, after critical study and analysis, most of the source data on saturated steam are in satisfactory accord.

CONTENTS

	Page
I. Introduction	412
II. General description of method and apparatus	413
1. Method	413
2. Apparatus	413
3. Résumé of theory of method	414
III. Description of calorimeter	416
1. Calorimeter shell	417
2. Circulating pump	417
3. Stuffing box	419
4. Electric heater	419
5. Envelope	420
6. Control bath	422
7. Thermometric installation	423
8. Throttle and reheat tube	426
IV. Accessory apparatus	427
1. Flow lines and control valves	427
2. Containers for water	429
3. Pump speed control	429
4. Timing devices	429
5. Pressure measuring instruments	430
6. Electrical measuring instruments	430
7. Weighing instrument	431
8. Thermometric standards	431
9. Purification of water	432
V. Description of measurements	422
1. Accounting for mass of water	433
2. Heat-capacity determinations	434
3. Latent-heat determinations	437
4. Evaporation factor	439
5. Thermal leakage	439
6. Pump energy	441

Page
VI. Results of measurements 441
1. Alpha experiments 441
2. Gamma experiments 468
3. Beta experiments 470
VII. Formulation 476
1. Formulation of calorimetric data 476
2. Derivation of heat content and entropy from calorimetric data 478
3. Discussion of accuracy 479
VIII. Acknowledgments 480

I. INTRODUCTION

The measurements here described were undertaken to meet a need for more data to be used as the basis for a steam table suited to present and prospective demands of steam-power engineering. The work was initiated as a result of the conference [1] of engineers and physicists which was held in Cambridge, Mass., on June 23, 1921. The program of experimental work undertaken by the Bureau of Standards was a part of a greater project which has been sponsored and largely supported by the American Society of Mechanical Engineers. Harvard University and Massachusetts Institute of Technology have cooperated in this project by undertaking definite programs of investigation.

The importance of international accord as to the basis of steam-power calculations has been recognized here and abroad. This has resulted in the international cooperation of engineers and investigators in the correlation of their work, with the object of ultimately developing a universally acceptable steam table.

In the program of securing new data for the revision and extension of the steam table the part which was undertaken by the Bureau of Standards is concerned with the energy changes which occur in the fluid, water, when a mixture of the liquid and vapor phases is subjected to changes of state. The thermal properties which characterize these changes may be determined by calorimetric measurements made upon samples of the fluid under its own vapor pressure, or, in other words, at the saturation limit. In the present work a systematic series of such calorimetric measurements has been carried out. A group of thermal properties has been determined which constitutes a calorimetric survey of the behavior of steam in the saturation region extending from 0° to 270° C. The theory of the experimental method employed and the analysis of the physical processes have been given in two publications,[2] of which the latter gives the more general and complete theoretical treatment. Brief descriptions showing the development of the design and construction of the equipment, the progress of the experimental work, and the tentative results obtained, have appeared from time to time as progress reports.[3] Because of the tentative nature of the results previously published, the work has been described only briefly. In this report of the measurements completed to date, a more complete account will be given of the design, construction, and use of the apparatus and of the reduction and formulation of the results.

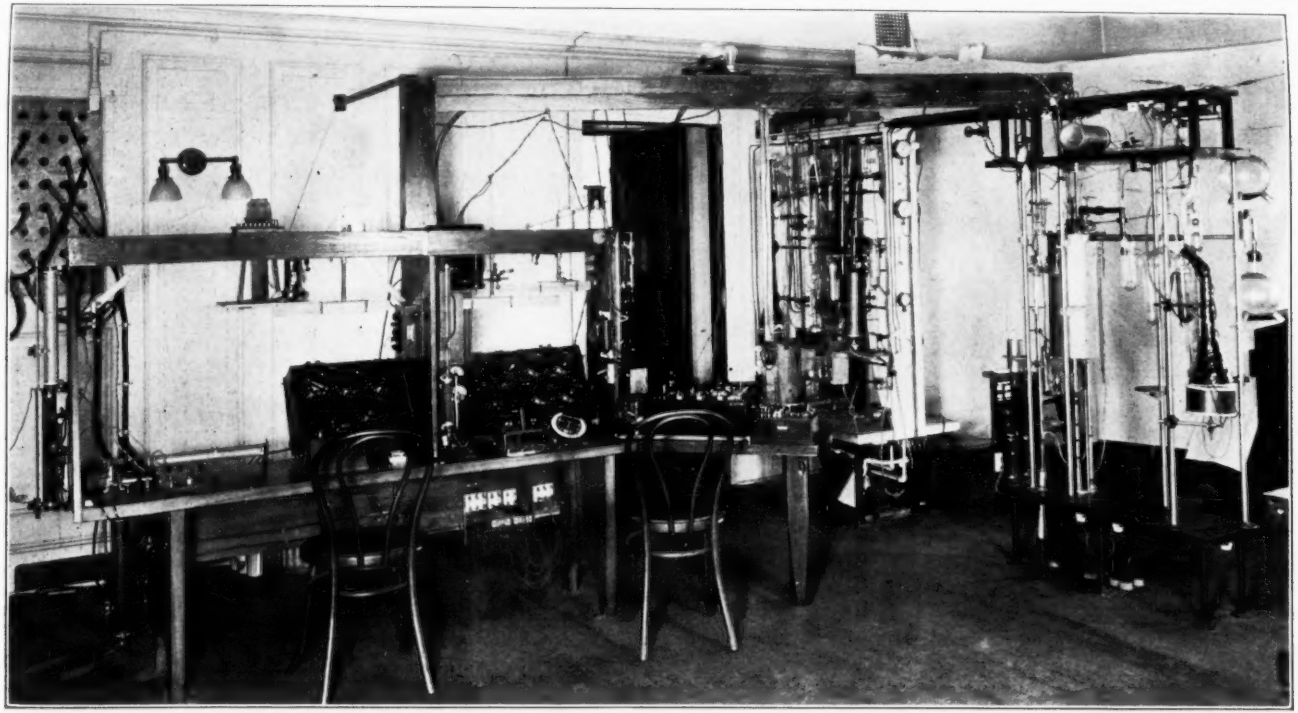
---

[1] Mech. Eng., **43**, p. 557; August, 1921.

[2] J. Opt. Soc. Am. & Rev. Sci. Inst., **8**, No. 4, p. 519; 1924; B. S. Jour. Research, **4**, No. 5, p. 609; 1930.

[3] Mech. Eng., **45**, No. 3, p. 168; 1923; **46**, No. 2, pp. 81, 83; 1924; **46**, No. 11a, p. 808; 1924; **47**, No. 2, p. 106; 1925; **48**, No. 2, p. 152; 1926; **49**, No. 2, p. 162; 1927; **50**, No. 2, p. 152; 1928; **51**, No. 2, p. 125; 1929; **52**, No. 2, p. 127; 1930.

U. S. Journal of Research, RP209



Electrical measuring instruments | Still for purifying water | Assembled calorimeter

FIGURE 1.—*General view of assembled equipment*

FIGURE 3.—*Parts of pump casing and calorimeter heater*

Recently a study [4] has been made of published source data from previous calorimetric work on water and steam in the saturation state. It is therefore unnecessary to include in this paper any of the details of that study, but the revised values and the appraisals there made serve as the basis for their comparison with the results of this present group of measurements. These results have been formulated into an exhibit of the calorimetric behavior of water as saturated liquid and vapor with which other groups of source data may be correlated. This formulation, starting with liquid water under its own vapor pressure at 0° C., extends up to 270° C., and for this range constitutes a consistent, coherent table of observed thermal properties of saturated steam, and may be regarded as an available foundation for a more extensive formulation of the properties of steam.

II. GENERAL DESCRIPTION OF METHOD AND APPARATUS

Before attempting to describe any of the details of design, construction, and operation of the apparatus, which, it must be admitted, is somewhat complicated, the general scheme will be outlined. A general photographic view of the equipment as assembled in the laboratory for operation is shown in Figure 1.

1. METHOD

The method makes use of a single calorimetric equipment by means of which measurements are made to determine several of the important thermal properties of the fluid. A sample of the fluid in a closed container at some chosen saturation state is heated electrically to some other chosen saturation state, or else is withdrawn either as saturated liquid or as saturated vapor. The energy required for each of these three processes is added and measured electrically. The amount of energy added per unit mass is characteristic of the particular experimental process observed. The group of measurements yields essentially the heat content or enthalpy, together with several other important properties, and establishes the thermal behavior of the fluid in the region covered by the survey.

2. APPARATUS

The apparatus consists essentially of a calorimeter which provides a place where a sample of water may be so isolated from other bodies as to enable its amount, state, and energy to be accounted for. The sample may be made to pass through a chosen, accurately determined change of state, while the accompanying gain or loss of energy is likewise accurately determined. The design of the apparatus provides for several such experimental processes selected for their physical simplicity and for their fitness to exhibit the thermal behavior of the fluid. The arrangement of the apparatus is shown in Figure 2.

A quantity of water, part liquid and part vapor, is inclosed in a metal calorimeter shell. The water is circulated rapidly about the interior in such a manner as to distribute heat and promote close approximation to thermal equilibrium. An electric heater continually bathed with flowing water provides a means of adding measured

[4] B. S. Jour. Research, 5 (RP210), p. 481; 1930.

energy which is speedily distributed throughout the calorimeter system. Outlets with valves provide for the introduction or withdrawal either of liquid or of vapor. Detachable receivers suitable for weighing are connected to the outlets to hold the samples of water transferred.

For confining the energy, the calorimeter is well insulated from the influence of external sources of heat and cold. In operation the temperature of an enveloping shell is kept very close to that of the calorimeter shell itself. The heat which passes by leakage to or from the calorimeter system is accounted for as a small correction which is determined. The energy consumed in circulation and added to the system as heat is another small correction which is determined.

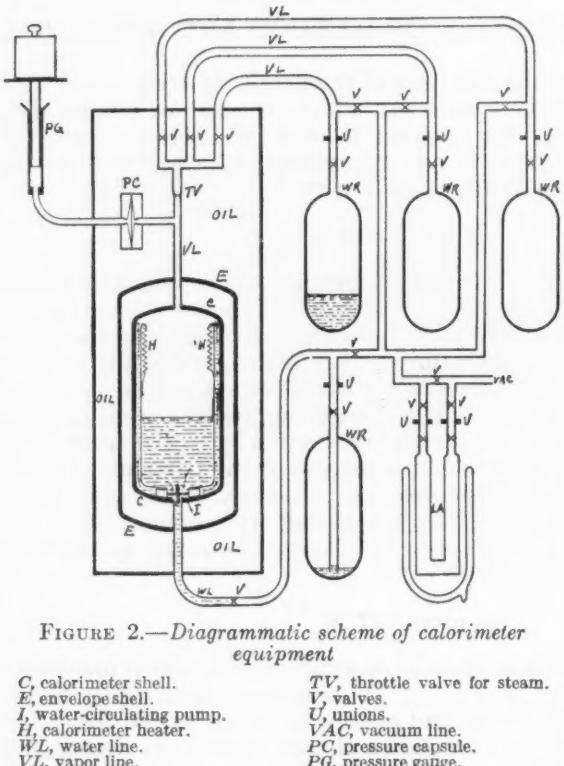


FIGURE 2.—*Diagrammatic scheme of calorimeter equipment*

C, calorimeter shell.
E, envelope shell.
I, water-circulating pump.
H, calorimeter heater.
WL, water line.
VL, vapor line.
WR, water receiver.
OIL, oil bath.
TV, throttle valve for steam.
V, valves.
U, unions.
VAC, vacuum line.
PC, pressure capsule.
PG, pressure gauge.
LA, liquid air trap.

Means are provided for observing the following quantities: (*a*) Temperature of the calorimeter and contents; (*b*) vapor pressure in the calorimeter; (*c*) mass of fluid contents of the calorimeter; and (*d*) energy added to the system, including electric energy converted to heat and the small corrections for thermal leakage and circulation.

The apparatus is designed to permit three special types of measurements to be made. In the ideal case of perfect manipulation and control of experimental conditions these would consist essentially of observations of the following processes: (*a*) Heating with fixed amount of contents (heat-capacity determinations); (*b*) isothermal expansion by adding heat, evaporating liquid, and removing saturated vapor (latent-heat experiments); and (*c*) isothermal expansion by adding heat, evaporating liquid, and removing saturated liquid.

3. RÉSUMÉ OF THEORY OF METHOD

By using the results of the published theory [5] the measured quantities may be expressed algebraically in terms of familiar thermal properties. The experimental determinations of heat capacity of

[5] B. S. Jour. Research, **4**, No. 5, p. 609; 1930.

ample of water give as a result the increase in the quantity $H - L\frac{u}{u'-u}$ ver the observed range of temperature, in which H and L denote, espectively, in energy units, the heat content of saturated liquid and eat of vaporization per unit mass, and u and u' denote specific olume of saturated liquid and vapor, respectively.

In the latent-heat experiments we measure the energy which is dded when water is evaporated and withdrawn as saturated vapor at onstant temperature. This amount of energy per unit mass is equal o $L + L\frac{u}{u'-u}$. The ratio $\frac{u}{u'-u}$ is the fraction of a unit mass vaporated but remaining within the calorimeter when unit mass is ithdrawn.

The quantity $L\frac{u}{u'-u}$ is complementary both to the determinaions of heat capacity and to the determinations involving vapor ithdrawal when the values of H and L are desired. This quantity s measured conveniently at any desired temperature by observing n supplementary calorimetric experiments of the third type the nergy required to produce the necessary evaporation when a certain uantity of saturated liquid is withdrawn.

Thus, the three different types of experiment yield values of three uantities referred to certain temperatures. These quantities, $H - L\frac{u}{u'-u}$, $L + L\frac{u}{u'-u}$, and $L\frac{u}{u'-u}$, are denoted by the symbols, α, γ, and β. From these are derived finally the values of heat conent of saturated liquid, H, heat content of saturated vapor, H', nd heat of vaporization, L. In addition to these three energy uantities, characteristic of the fluid, there also may be derived from he calorimetric data the entropies of the saturated liquid and vapor; nd by use of vapor-pressure data, obtained from other sources, pecific volume and internal energy may be calculated.

The properties of water at the saturation limit which may be erived from the calorimetric data and the formulas by which these erivations are made are as follows:

$$H = \alpha + \beta$$

$$H' = \alpha + \gamma.$$

$$L = \gamma - \beta$$

$$\Phi = \int \frac{\alpha d\Theta}{\Theta^2} + \frac{H}{\Theta} = \int \frac{d\alpha}{\Theta} + \frac{\beta}{\Theta}$$

$$\Phi' = \Phi + \frac{L}{\Theta}$$

in which the following notation is used:

H = Heat content per unit mass of saturated liquid $(\epsilon + \pi u)$, referred to an arbitrary zero.

H' = heat content per unit mass of saturated vapor, referred to the same zero as H.

L = heat of vaporization per unit mass $(H' - H)$.

u = specific volume of saturated liquid.

u' = specific volume of saturated vapor.

$$\left.\begin{aligned} \alpha &= H - L\frac{u}{u'-u} \\ \beta &= L\frac{u}{u'-u} \\ \gamma &= L\frac{u'}{u'-u} \end{aligned}\right\} \text{measured quantities.}$$

Θ = temperature in centigrade absolute.

ϵ = internal energy per unit mass.

π = vapor pressure at saturation limit.

Φ = entropy per unit mass of saturated liquid, referred to an arbitrary zero.

Φ' = entropy per unit mass of saturated vapor, referred to the same zero as Φ.

III. DESCRIPTION OF CALORIMETER

The term "calorimeter" will be used here to denote that portion of the apparatus where the observed thermal process occurs. It is the part from which external influences are so isolated that the experimental processes may be accurately controlled and observed. The calorimeter is thus the relatively small part of the apparatus within which we may account accurately for energy added, amount and state of matter, and work done. It forms the nucleus around which the whole experimental equipment is developed.

The calorimeter was designed so that each of the three thermal processes previously mentioned could be separately observed. From these observations the corresponding group of thermal properties of water can be derived. Several general principles have aided in developing the design. These precepts may be enumerated as follows:

(*a*) A preliminary analytical study throws important light upon the applications of the thermal processes leading most directly to the desired results.

(*b*) Simplification of the experimental processes by refinement of the details of equipment and manipulation makes departures from the ideal experiment small or negligible, and thus promotes reliability.

(*c*) Advance consideration of the relative importance of individual refinements is more to be desired than makeshifts to account for and eliminate inconsistency of results.

(*d*) The apparatus should be moderately proportioned so as to promote accuracy and facilitate construction, assembly, and operation.

(*e*) The best available materials and workmanship are most economical in the end.

(*f*) Proof tests of materials, particular features of design, and of partly assembled portions of the whole reduce hazards to the completion of the work.

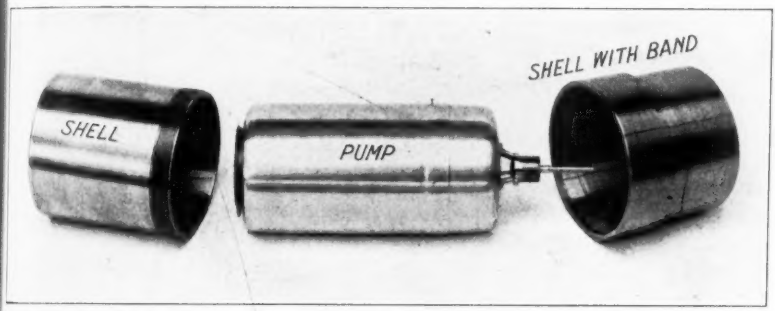


FIGURE 4.—*Calorimeter pump and shell*

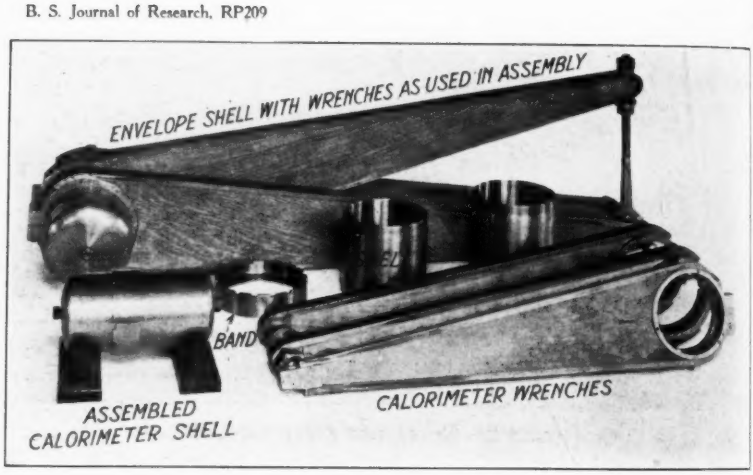


FIGURE 5.—*Wrenches and manner of assembling shells*

These principles may appear so obvious as to need no mention, they suggest ideals to be sought and are recalled at this point to icate a background against which closer details may be viewed in per perspective.

1. CALORIMETER SHELL

The purpose of the calorimeter shell shown at *C* in Figure 11 is to vide a receptacle or reservoir for the sample of water under ob- vation. This shell is cylindrical in shape, having spherical ends, d is made of an alloy of 80 per cent copper and 20 per cent nickel. contains, in addition to the water, the parts which serve as operat- organs. These consist of a circulating pump, electric heater, etc., d will be described presently. To provide for installation of these ts, the shell is made with a joint normal to its axis. The two main tions of the shell were shaped by cold drawing. Each is accurately chined, one with a right-hand and the other with a left-hand ead at the joint. The parts are brought together by a Monel- tal band threaded correspondingly. The joint is made tight by pressure which a tongue on one portion exerts on a gold-wire sket lying in a groove in the other portion. To assemble this nt three special powerful wrenches, shown in Figure 5, were vided. Two of these are clamped about the smooth cylindrical faces, while the third wrench engages a series of rectangular tches in the Monel band. The two clamps are yoked together at outer end, and a threaded draw bar provides the driving force in final closure of the joint. In this operation sufficient initial stress st be developed in the band to insure a perfect seal against the por pressure of the water at any subsequent operating tempera- re. The amount of force with which the shell is drawn together s determined by making actual proof tests with saturated steam a higher temperature than the experiments are intended to reach. expected, these proof tests showed that the joint acted as a safety lve which would open at a rather definite steam pressure and close ain after the pressure was moderately relieved.

The interior of the shell is heavily plated with silver, burnished er each successive plating. This is for the purpose of avoiding ntact of the water with the base metal of the shell, silver being re resistant to hot water than the copper-nickel alloy. The terior is likewise silver plated to give it a bright surface.

The various plugs and fittings which serve as ducts for tubular nnections with the outside and for electric power connections are ade of alloys of silver and sealed with gold gaskets in tongue-and- oove joints.

2. CIRCULATING PUMP

The purpose of the circulating pump is twofold. It maintains a pid circulation of the liquid about the walls of the calorimeter shell r distributing heat and thus promotes thermal equilibrium. It ovides at the same time a source of liquid at the top of the calo- meter for keeping the heater surface bathed with water spread out a thin, flowing stream.

Vigorous circulation lessens the time required to equalize the tem- erature of calorimeter and contents and permits observations of eady initial and final temperatures to be made promptly.

Another advantage of the rapid distribution of heat is that dur the time when heat is being added electrically, temperature gradie on the calorimeter surface are kept small. The mean temperatu of the surface may be obtained with reference to the opposed en lope surface by means of distributed thermoelements for accur evaluation of the thermal leakage.

The method of bathing the heater by a continuous thin flowi layer of liquid brings the evaporating surface close to the ener source, and thereby accomplishes quiet evaporation, producing d saturated vapor with very little distrubance of temperature in t entire system. This feature will be discussed later.

The construction of the pump is indicated in Figures 3 and It is of the centrifugal type, specially designed for the requiremen of this particular case. The pump circulates about 6 liters of wa per minute, the equivalent of the entire contents passing arou every 5 seconds. The flow circuit divides at the top, the lar part following the wall of the shell and the rest flowing through port, down over the heater, and thence down to the inside stora space. To circulate the two streams, one of large flow and low he and the other of small flow and greater head, the pump wheel impeller is made in two parts, rotating together and delivering in the same casing. As a result of tests of the characteristics and ef ciencies of a series of model pumps, this final design combining t stages in parallel, each of different characteristics, was developed a was found to give satisfactory heat-distributing capacity with tolerably small power input.

The energy consumed in the pump is dissipated as heat added the calorimeter system and is objectionable if its amount is indete minate or too great. Too large a pump energy input would interfe with the accurate observation of the initial and final temperature Too much fortuitous variation in the pump energy would impair t accuracy of accounting for energy from this source.

The normal speed of the pump wheel is 900 r. p. m. This spe was changed in certain experiments as found desirable. The meth of speed control will be indicated later. The power input is dete mined calorimetrically and varies from 0.05 to 0.10 watt, dependi on controlled conditions. The flow in the inner circuit over t evaporator and through the stage which maintains the head f keeping the main flow channel full is about 1 liter per minute. T flow in the main channel is about 5 liters per minute. The efficien in pumping the water from intake to discharge at the top of the cal rimeter was found to be about 28 per cent. The construction of pump of this size and character designed to operate continuously i water up to 300° C., with no other lubrication of the running par than that furnished by the water, built of materials which would b unaffected by the action of the water, involved some interesti problems.

The impeller runs on ball bearings of iridium alloy. The ball are about 1.2 mm in diameter, 10 balls in the lower and 7 in th upper bearing. The main part of the runner is built up of silve palladium alloy. The shroud and clearance ring of the upper stag are made of one piece of silver-gold alloy riveted to the runne The vanes are machined to stream-line curves. The lower stage ha neither shroud nor clearance ring.

The five parts of the pump casing and flow channels are formed of pure silver. These parts go together with well-fitting slip joints fastened, where necessary, with pins. The entire pump, discharge tube, and flow-channel casing form a unit which, when assembled, is borne rigidly within the calorimeter shell on three supports of stream-line form, machined from a solid piece of silver-gold alloy, which fits the central opening at the bottom of the shell.

The pump runner is driven by a square on the lower end of the main runner shaft which engages the square in the upper end of the tubular propeller shaft of silver-palladium alloy. This propeller shaft extends down through the lower tubular support of the shell and on down to the stuffing box where it engages the stuffing-box shaft of hardened tool steel with another square joint.

3. STUFFING BOX

The stuffing box, built to provide for the rotation of the drive shaft of the calorimeter pump without permitting leak of water by it, is shown at *WSB* in Figure 11. A cylindrical recess 5 mm in diameter and 12 mm deep in the Monel body was fitted closely with two small cup-shaped packing retainers. The one which goes above the packing is of silver-palladium alloy and the one below of phosphor bronze. These retainers fit the 1-mm hardened-steel drive shaft within 0.01 or 0.02 mm on the diameter, so that very little space is left through which the packing can flow. The packing consists of soft kid-leather washers impregnated with paraffin. Pressure is transmitted to the packing in the recess by means of an appropriate number of cupped washers of spring steel. These are compressed to the desired degree by means of a gland threaded into the body of the stuffing box. In order that there shall be no leak it is necessary that the hydrostatic pressure in the packing be greater than the vapor pressure in the calorimeter. To prevent undue wear on the pump shaft the number of spring washers, the method of combining them, and the amount of deformation imparted to them are adjusted to meet the needs of the experimental conditions. To avoid the difficulties of finding a packing which would be satisfactory at high temperatures, the stuffing box is placed outside the lagging and water cooled. The size of the pump shaft where it engages the packing was reduced to 1 mm to cut down the wear. Below the packing the shaft is larger, and is provided with a ball bearing to take the downward thrust. The race for this bearing is attached to the outside of the body of the stuffing box by a threaded joint and can be removed readily for examination of the packing. A brass collar prevents undue upward motion of the shaft. Power for driving the pump is supplied from below, as will be more fully described later, and transmitted to the pump shaft by a hollow drive shaft having squared slip joints to provide easy assembly yet positive drive.

4. ELECTRIC HEATER

The electric heater furnishes the means by which the major portion of the measured energy is added to the calorimeter system. So far as the heat-capacity experiments of the first type are concerned, no extraordinary restrictions as to characteristics of this part are necessary, as the exact path by which the change from an initial to a final temperature occurs is of no importance if the energy account is faith-

fully kept. In the case of evaporation experiments, and particularly those of the second type, much may depend on the way in which the energy is supplied and utilized in the evaporation process. The question as to the actual state of steam used in latent-heat measurements is the moot point which has frequently been raised as affecting the dependability of published values. If the energy could be supplied exactly at the surface where it is required for evaporation, none of it would go to superheating either the liquid or the vapor. Evaporation would then proceed quietly and dry saturated vapor would be produced. In this calorimeter the electric heater, which is, in fact, an evaporator, has been developed to effect quiet evaporation and the formation of dry saturated steam with very little disturbance of thermal equilibrium in the calorimeter and contents.

The evaporator heater as installed is shown in section at *H* in Figure 11 and photographically in Figure 3. In this electric heater a resistance wire of constantan 0.4 mm in diameter, with gold leads of the same size, forms the resistor. This resistor is insulated by embedding it tightly in dry clay which completely fills the pure silver tubular sheath. The portion of the sheath containing the resistor is flattened to a thickness of about 2 mm. The end portions containing the gold leads are drawn to a diameter of about 2 mm. The flattened portion is wrapped spirally with a strip of pure silver fine-wire gauze, fastened by spot welding at a number of points. The flat resistor portion is then bent into the final helical form as shown and the leads bent so as to pass downward and out of the shell through the fitting.

The purpose of the gauze wrapping is to insure even distribution of the stream of water which flows through the annular port, and thence down as a thin sheet enveloping the evaporator.

The resistance of the completed heater is about 10 ohms. The insulation resistance between the resistor element and the silver sheath was found to be about 90 megohms when cold.

The evaporator when installed is held in its central position just below the water port by a 3-armed silver support carried on the central portion of the discharge tube of the pump. The water is led from this port by guides of silver gauze and brought to the very top of the evaporator. The excess of liquid which flows off the evaporator is led quietly down into the central reservoir by a similar guide or apron of gauze.

5. ENVELOPE

The chief purpose of the envelope which surrounds the calorimeter shell is to provide a receptacle in which the shell may be installed to isolate it from adventitious or fortuitous sources of energy.

We may regard the space between the calorimeter shell and the envelope as a barrier to heat flow, pervious to only a slight extent. The necessary metal connections between the calorimeter and its surroundings furnish other restricted channels for heat flow. The thermal-leakage rate may be made small by refinement of construction, but can only be annulled completely by avoiding temperature difference. This may not be actually possible, but by first making the thermal insulation very good and then in operation keeping the temperatures under control it is possible to keep the heat leak extremely small in all cases and to account accurately for the unavoidable small heat leak which does occur. Provision has been made for both these measures in the present calorimeter, as will presently be shown.

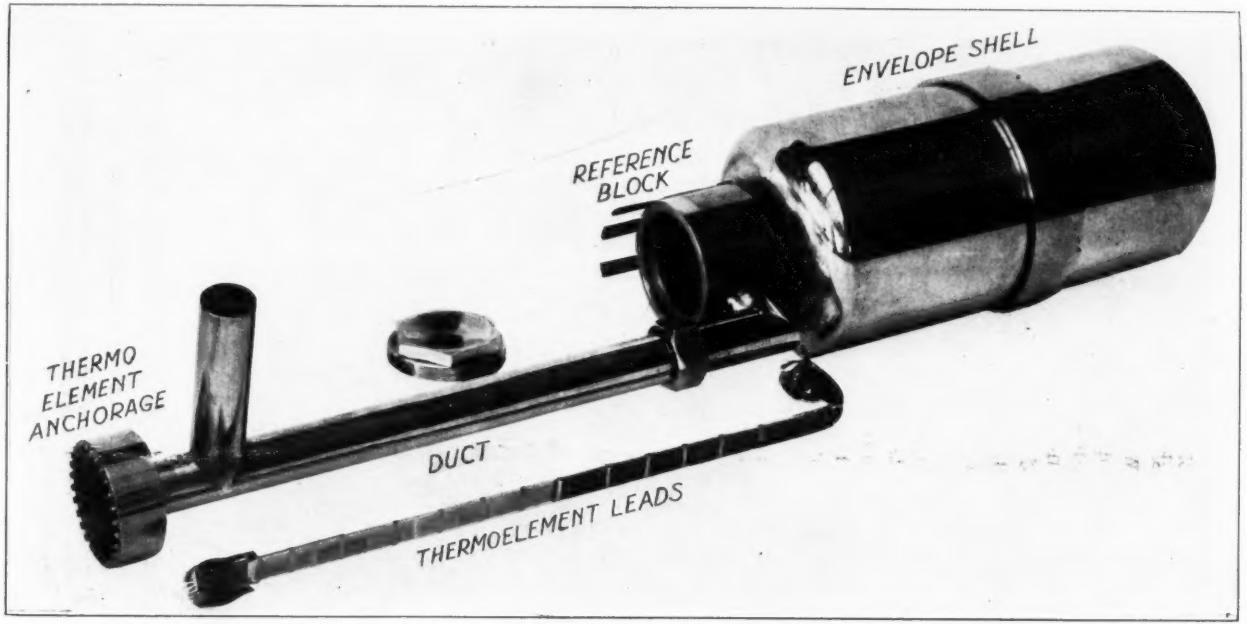


FIGURE 6.—*Envelope shell with reference block, duct, and thermoelement leads*

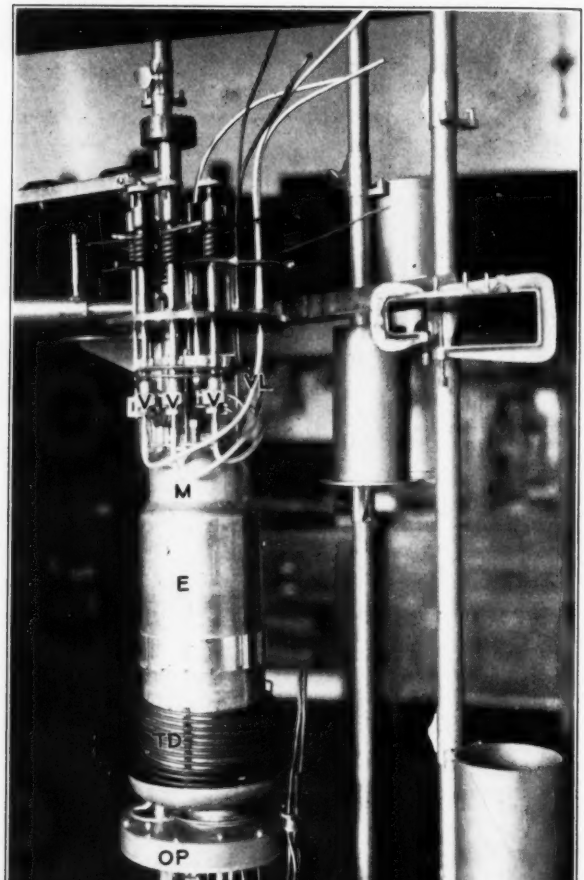


FIGURE 7.—*Partly assembled calorimeter*

E, Envelope shell; *M*, mantle for reference block; *TD*, thermoregulator dilatometer; *V*, shut-off valves; *VL*, vapor lines; *WSB*, water stuffing box; *OP*, oil pump.

The envelope is shown at *E* in Figure 11. This outer shell is very similar in construction to the shell of the calorimeter. It is of the same material, made in two parts, assembled in the same manner. This shell is made strong as a precautionary measure in case the inner shell should fail to hold the water sample under pressure.

The calorimeter shell is supported axially within the envelope by means of two tubes of silver-palladium alloy, one at the top and one at the bottom. Besides furnishing strong stiff supports, these tubes serve also as channels for transfer of fluid to or from the calorimeter, either as liquid or vapor. The lower tube also incloses the propeller shaft of the circulating pump. The upper tube serves as an opening through which a tool may be introduced for adjusting parts. The metal of these tubular supports was chosen because it possessed the desired characteristics of resistance to action of hot water, strength, thermal resistivity, and satisfactory workability.

To avoid the danger of injury to the delicate supporting tubes by accidental shock to the system when in place, six metal pegs are fixed in the wall of the outer shell, extending radially inward nearly to the surface of the inner shell but not touching it. These are placed in two planes near the top and bottom of the cylindrical part of the inner shell and are so adjusted in length as to prevent any eccentric displacement which would endanger the supporting tubes.

Thermal leakage may take place by either of four types of heat flow, namely, radiation, solid conduction, gaseous conduction, and convection. The first of these, radiation, is made small by silver plating and polishing the outer surface of the calorimeter shell. This finish has a tolerably low emissivity in the temperature range of these experiments.

Conduction through the metal parts extending across the insulating space is kept within bounds by choice of materials and proportions of the necessary supporting tubes and electrical leads. The supports have already been described above. The electrical leads which contribute to thermal leakage comprise 21 chromel and 14 copel thermoelement wires each 0.1 mm in diameter. Each of these materials has low thermal conductivity, and these leads contribute little to the total heat leak. The electric current and potential leads are a larger factor. These are of gold wire. The current leads are about 0.6 mm in diameter and about 4 cm long. The potential leads are about 0.2 mm in diameter and 8 cm long. They are disposed of in the envelope space about as shown in Figure 11.

Heat leak by gaseous conduction and convection was dealt with at first by providing means for evacuating the envelope space to a low residual-gas pressure of about 0.0003 mm of mercury. At this pressure the heat leak by this path is insignificant. The calorimeter was operated this way during much of the earlier work at moderate temperatures. At temperatures of 200° C. and over, trouble developed due to leaks appearing in the envelope system surrounded by oil. Presence of the small amount of oil which penetrated into this evacuated space produced thermal effects which were baffling until finally traced to their cause. After contending with this difficulty for some time it was decided to discontinue the evacuation of the envelope. Instead, it was filled with nitrogen at about atmospheric pressure. This practice gave a slightly greater thremal-leakage coefficient, but inasmuch as this coefficient was determined as a

part of the systematic routine and the actual heat-leak corre made in every experiment, a small percentage change in an alr extremely small correction term was of no consequence.

Supplementing the above-mentioned features of thermal insula of the calorimeter there is a thermometric device for indicating relative temperatures of calorimeter and envelope surfaces and a means for controlling these temperatures. The thermoelem which serve for the first of these form a part of the whole ther metric system which will be described in detail presently. The mal control bath which surrounds the envelope is the medium effecting temperature control will next be described.

6. CONTROL BATH

The control bath as shown in Figure 11 is contained in a b casing, which, when assembled, supports the calorimeter in its velope, through the axial connecting tube at the bottom. The tom of the bath casing is a circular brass plate which is supporte three flattened tubular columns. These columns rest on a l deck, which is a part of the outer casing which holds the lagg This lower deck is borne on a main support of three columns w thus carry the main calorimetric unit.

The somewhat involved construction of these inclosures was n necessary in order to provide in advance for an assembly or disn tling without unnecessary disarrangement of delicate or remote p This precaution has proved a great advantage, when, in operat either failure of a part or need for change or readjustment have ne sitated access to more or less remote points inside.

A mineral oil of suitable viscosity and flash point is circulate the bath by the path indicated in Figure 11. A centrifugal p drives the oil about this circuit. Each of four electric-heater u supplies energy for some specific purpose. The one for principal supply furnishes most of the heat which escapes to the outside part of that which is used to raise the temperature of the bath. so-called "main heater" is located on the outer wall of the b casing. It is made of nichrome wire, 0.8 mm in diameter, wo first in helical form, then flattened to a ribbonlike coil. After outer wall of the bath casing had been covered with a thin laye alundum cement baked hard, this heating element was wound and another coat of alundum cement applied to hold it in pl The two windings have a resistance of 10 ohms each and can be either singly, in series, or in parallel. This heater will, of course, produce a quick response in the bath to a change in current. To vide for quick response an "auxiliary heater" is installed in the u portion of the oil space above the envelope shell. This auxil heater is a copper-sheathed, clay-insulated unit similar in princip the calorimeter heater, but proportioned and shaped for this pl Its resistance is about 10 ohms.

To provide for automatic regulation of the bath temperatu third or "regulating heater" of 10 ohms, similar in construction to one just described, was installed in the oil-return flow just ahea the pump intake. The current in this heater is automatically va to maintain constant temperature in the bath by the thermoregul which will soon be more fully described.

fourth heater called the "central heater" is an auxiliary heater ched to the fitting on the central tube at *CH* in Figure 11. This bles the operator to keep the upper end of the central supporting e of the calorimeter at a higher temperature than the calorimeter, s to avoid condensation. The central heater is of the clay-insu- d copper-sheathed type, wound spirally on a core of copper, to ch it is hard soldered. This core is clamped to the fitting which it esired to heat.

refrigerating coil is installed in the bath to permit operation at peratures down to 0° C. This consists of a tube, as shown at in Figure 11, and may be used to carry carbon dioxide, cooled by ttling from high pressure. By connecting the refrigerating coil he water supply it can be used to cool the system after experiments igh temperature.

The thermoregulator is actuated by an oil dilatometer in which the iation of temperature causes motion of a mercury column in a ll tube, thus making or breaking an electric circuit. This impulse ates a relay which effects the change in heating current. The rmoregulator is of the selective-setting type long used in this oratory. When heating up, a valve is left open, permitting the pe of expanded fluid. When the desired temperature is reached valve is closed, heating currents are readjusted, mercury contact lly set, and the temperature is then automatically held.

The dilatometer of the regulator is a long thin-walled tube wound helical form and installed in the oil stream where it meets the velope shell, as shown at *TD* in Figure 11.

The insulating material used for lagging is calorox. No attempt s made to make the heat leak from the bath very small by using at bulk of lagging. It was thought more expedient to conserve ce and weight by wasting a little more electric power. The outer ng is water-cooled to keep it from getting too hot to the touch.

The various connections extending up more or less rigidly from the rimeter unit emerge through easily fitting tubular wells in the top he control-bath casing. This permits near closure of the oil space, the same time allowing for differential expansion of the parts. xible connections are brought out through tight fittings. Special ls are provided through which the resistance thermometers are erted into their receptacles, yet to be described.

The control bath is designed to conserve space and heat capacity utilizing the circulating oil as a medium for rapid transfer of heat her than as a heat reservoir. It is necessary to provide for the nge in volume of the oil over the temperature range used. An let at the top leads through a water-cooled tube to a trap with two reservoirs, each of 3 liters capacity. The supply flask is above, erted, with spout below the overflow. The other is below to re- e oil which overflows. This arrangement keeps the oil level at a nite height in the wells, whether temperature is rising or falling.

7. THERMOMETRIC INSTALLATION

Temperatures at various chosen points on the calorimeter and velope are observed by the combined use of platinum resistance rmometers and thermoelements. A heavy copper reference ck located in the bath at *R* in Figure 11 serves as the thermal union

between the resistance thermometers and the reference junctio the thermoelements. The thermometers thus measure the tem ture of the reference junctions, and the thermoelements indicat small temperature differences which exist between the reference and the principal junctions located at the chosen points.

The three thermometers fit into copper receptacles which are soldered to the reference block. Thirteen thermoelements, each ing reference junctions on this same block, have principal junctio points on the calorimeter shell and its envelope, as shown in F 11. Each element is made of 0.1 mm. diameter chromel and wires, stranded so that two copel and three chromel wires lead t junctions. Each element has three junctions—a principal one a place where indication of the temperature is desired and two refe junctions on the reference block. From these gold wires lead t outside. A diagram of a single thermoelement is shown in Figure

Copel-chromel elements were chosen because of their comparati high thermoelectric power and relatively low thermal conductivit

The reference block is especially designed to avoid temper gradients and keep all the reference junctions and resistance mometers at same tempera It is attache the calorimete velope throu short tube of h copper-nic From this blo similar tube tends laterally thence by a turn vertically ward and out o bath, where it

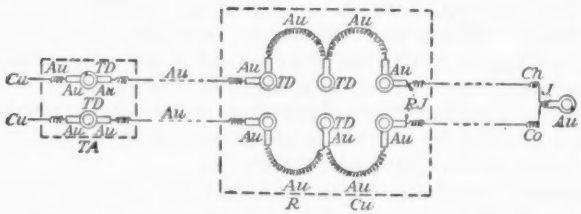


FIGURE 8.—*Diagram of thermoelement*

J, principal junction; *RJ*, reference junction; *R*, reference block; *TD*, thermoelement lead tie-down; *TA*, thermoelement lead anchorage; *Co*, copel wire; *Ch*, chromel wire; *Au*, gold wire and terminals; *Cu*, copper.

minates in an air-tight insulating seal (*S*, fig. 11) for the wires, which led out through this duct. A side connection near the top is use the evacuation of the envelope or the filling with gas. The refer block itself is a heavy cylindrical mass of copper with circular s inside like an amphitheater. These steps afford space for attac the reference junctions of thermoelements. Three flat tub copper receptacles are attached to the block to receive the spatul ends of the resistance thermometers which are inserted from ab This well-conducting copper mass forms a thermal union betwee thermometers and the thermoelements in which only extremely s temperature gradients can persist.

However, if left entirely unprotected from the direct influence o oil stream, whose temperature is controlled by the automatic the regulator, this block would experience sensible fluctuations of tem ature from the controlled mean, which would interfere with pr observations. In order to damp out these fluctuations there is vided a mantle in the form of a figure of revolution fitting the cyli and the envelope shell at *M*, Figure 11. It moves vertically in gu so that it can be placed as shown or raised to a higher level. Whe the upper position the oil passes within the mantle and bathes reference block directly. This is the proper position when the m temperature of the bath is being changed. When steady temperat

o be observed the mantle is lowered, thus keeping the reference
more remote thermally from the circulating oil and obliterating
eriodic fluctuations, at the same time allowing the block to follow
nean temperature of the oil.

r insulating and supporting the thermoelements within the en-
e, where this can not be accomplished merely by spacing the
wires, mica is used. All the junctions are insulated with mica
t for the principal junctions of Nos. 9 and 10, which are soldered
tly to the central tube, and No. 12, which is assembled without
ation for test purposes. By making suitable connections outside
thermoelements can be used either as individuals for survey of
erature distribution or in groups to indicate average surface-
erature difference for heat-leak control. The group of five on
calorimeter can
sed in series to
the calorimeter
erature to the
tance thermom-
s.

he 28 gold wires
ng out from the
ence junctions
ereference block
carried through
lticellular duct
lt up of mica
s in which each
has its own pas-
way. The wires
h lead down-
d from the refer-
block to the
cipal junctions
guided and sup-
ed by threading
ough appropriate
strips of mica.
method of at-

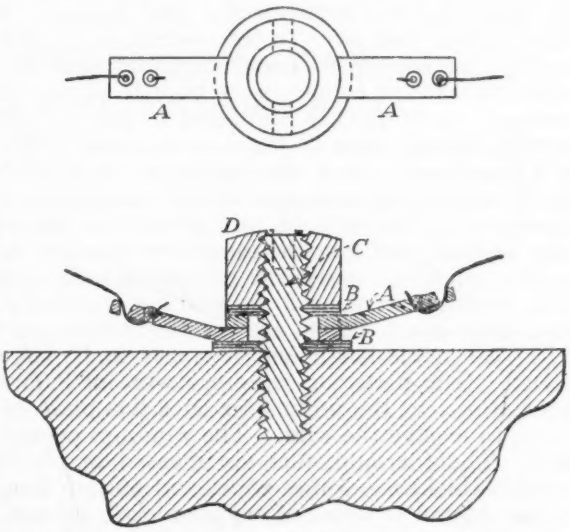


FIGURE 9.—*Details of thermoelement attachment*

A, gold terminal of thermoelement wire, lead, or junction; *B*, mica insulating washers not less than 0.1 mm thick; *C*, threaded stud; *D*, nut.

ing junctions to the metal parts so as to insure electric insula-
and provide at the same time good thermal union is shown
igure 9. The gold terminal to which are hard soldered the
wires forming the junction is clamped firmly between mica
hers to the metal surface under a nut threaded to a stud. By
same device connections are made between the gold wires
the reference junctions, simply leaving out any mica washer
between the gold terminals. Thermal "tie-downs" of the gold
s are made in the reference block to intercept lead conduction
h otherwise might reach the reference junctions and vitiate their
cations. Each wire is twice tied down before connecting with its
rence junction, thus reducing the effect of lead conduction from a
sible error of nearly a degree, in an extreme case, to about one
-thousandth of this amount. A total of 80 tie-downs find place
hin the reference block, and a total length of about 6 m of bare

wires, coiled in helical spirals, is accommodated in the 32 cm³ of s within this block, requiring considerable care in stowage to keep all clear of each other. After assembly the whole system of insu thermoelements showed an insulation resistance of several meg to the calorimeter unit at 500 volts.

The thermoelements are made up of fine stranded wires so they will have appropriate resistance and still be sufficiently fle to be manipulated into suitable shapes for stowage. The total s resistance of the group consisting of elements Nos. 1 to 5, inclu is about 100 ohms. This resistance gives critical damping wit potentiometer and galvanometer used for observing. The resist of the other combinations used are made up to similar total v by series resistance coils on the instrument board.

The copper ring (*TA*, fig. 11) furnishes an isothermal ancho for the junctions between the gold lead-out wires and the co wires which lead over to the instrument board. These circuit entirely of copper to avoid parasitic thermal emf's. Two sp switches, each of copper, were built to permit the individual the elements to be quickly connected to the potentiometer in the de combinations. One of these is a double-pole 12-throw dial sw and the other a quick double-throw 6-pole knife switch. Where dered joints were made, special care was taken to insure against the gradients in the joints. Every precaution was taken to reduce p sitic thermal emf's in the measuring circuits to a negligible amo

Four platinum resistance thermometers, specially constructed this purpose, were used as working standards for the tempera measurements. These are of the 4-lead potential-terminal t They are made small and compact to fit the receptacles descr above. The platinum windings were of 0.05 mm diameter, wo seven turns to the millimeter on a flat plate of mica notched at edges to receive the wire. The windings occupy a length of abou mm. The thermometers are incased in platinum sheaths 0.5 outside thickness, 5 mm wide, and 60 mm long. These sheaths hard-soldered to tubes of copper-nickel, 3.2 mm in diameter, thr which the gold-lead wires threaded through mica strips are led ou the seals at the top, where copper wires are joined on.

The platinum windings were annealed by flashing, using an ele current of short duration sufficient to heat the wires to redness mentarily.

The thermometric reference block is closed at the top by a flex annular diaphragm of silver to allow freedom for differential expan between the outer envelope and the suspended calorimeter shell its supporting tubes. The top of the block is terminated by a M ring hard-soldered to the copper, having a blunt-edged flange u which the silver diaphragm is clamped by the threaded nut bea against a washer. At the inner edge the diaphragm is simil clamped to the fitting which joins the supporting tube below connects with the distributing tube above, through a union.

8. THROTTLE AND REHEAT TUBE

This device has not been used up to the present time, but as it installed in the calorimeter from the first assembly and had some fluence on the design, although left inoperative, it will be briefly scribed. The extension of the silver-palladium outflow tube wi

alorimeter is threaded in the lower portion of its length with a of 80 threads to the inch. A plug of silver-gold alloy is fitted is thread so that it can be placed anywhere in the threaded part. il consisting of 170 cm of silver tube is connected at two points e outflow tube. By placing the plug between these points, vapor ng out of the calorimeter is first reduced in pressure and tempera- as it leaks by the plug threads, and then flows through the coil, e it is reheated by absorbing heat from the saturated vapor which unds the tube. This is the arrangement provided for a fourth of experiment in which the heat content of superheated vapor ld be determined.

s the calorimeter was used in the first three types of experiments, hrottling plug was left out entirely, leaving free passage for vapor he outflow tube.

IV. ACCESSORY APPARATUS

1. FLOW LINES AND CONTROL VALVES

he flow lines provide connections between the calorimeter and the ide receivers and are used to conduct the flow in the transfer of to or from the calorimeter. The lines at the bottom provide for introduction and withdrawal of liquid, while those at the top are in the withdrawal of vapor. Figure 2 shows diagrammatically various paths along which liquid and vapor can be conducted and elative positions of the control valves.

he valves used in the flow lines are all of the diaphragm type, ch permits motion for operation without the use of packing and be described later. Part of these can be operated as shut-off es and two as throttles for reducing pressure and controlling rate low.

ll flow lines are of silver or silver-palladium tubing. Those ch are at the pressure existing inside the calorimeter are of silver- adium, except one small silver tube at the bottom. This bottom e emerges from the side of the lower supporting tube, in the ing space, and leads downward near the stuffing box to the ide, as shown at *WL* in Figure 11. It serves for introduction emoval of liquid and is the only connection to the calorimeter ch has to be broken for dismantling the control bath. The silver- adium exit tube at the top of the calorimeter has two horizontal nches, one leading to a throttle valve and one to a pressure- ismitting device or pressure capsule, which will be described later. m the throttle valve a silver-palladium manifold tube leads to ee shut-off valves located in the control bath. From each of se a comparatively large silver tube leads out through the top of control bath and the lagging to a silver tempering coil which is vided with means for evacuation, through a diaphragm valve. e liquid line at the bottom leads through a diaphragm valve which es either as a liquid throttle or shut-off, to a similar tempering . All four tempering coils terminate in unions which fit the eaded portions of the valves on the containers for the water. All r vacuum valves lead to a common vacuum line, which is pro- ed with a metal trap in which water remaining in the connecting s can be caught and weighed.

The diaphragm valves already spoken of were designed to elim the use of packing. One of these will be described to illustra feature. In the section shown at *VV* in Figure 11, it may b that the action which opens and closes the valve is the v motion of a stem relative to a seat. The face of the stem is silver disk, and the seat in this type is a rather blunt but machined edge of silver-palladium alloy. Longitudinal mot the stem is permitted by an annular silver diaphragm of 0. thickness, clamped to seal tightly near the outer and inner Rotation of the stem is thus prevented. The portion of the outside the diaphragm is a cylinder fitting freely in a recess valve bonnet, so that the stem moves perpendicularly to the of the seat. Excessive flexure of the diaphragm is prevented metal support behind it and by limiting the travel of the stem this type of valve used on the containers and in the vacuum the motion is imparted to the stem by a differential thread ar ment. The differential screw has a square end which can be t by a detachable key.

Each of the three shut-off valves in the bath, one of wh shown at *V* in Figure 11, is of this same diaphragm type, b motion is imparted to the stem in a different manner. These have to be opened and closed as nearly instantaneously as po and no intermediate positions in the motion are required. T fore, instead of the differentially threaded stem, an entirely dif mechanism was designed to accomplish this purpose. Their are attached to vertical struts, leading outside the control ba a spring and lever system shown at *VM* in Figure 11. By m of the adjusting screws illustrated the mechanism can be s that any desired force of the stem on the seat will be furnish deformation of the spring lever, *SL*. It is evident from the di that by a single motion of the operating lever, *OL*, the valve c completely opened or closed. The provision by which these o tions are automatically carried out at a signal from the sta clock will presently be described.

The shut-off valve in the liquid line was changed during liquid-withdrawal experiments from the type shown at *W* Figure 11 to a type similar to the vapor shut-off valves in the co bath. Provision was made for the remote control of a slow-m screw which actuated the handle of the mechanism. The op of the valve could thus be controlled to regulate the rate of drawal of liquid.

The vapor throttle valve is similar to the shut-off valves, bu cause of the fineness of operation demanded of it, certain ch were necessary. The seat is made flat with a 0.5 mm apertur the silver disk on the stem is made slightly conical where it en the seat. The operating mechanism outside the oil bath was ch to the form shown in Figure 11 and was provided with a slow-m screw to operate the valve handle. This slow-motion screw is ated from the instrument table by a positive mechanical co The spring lever was replaced by a heavier brass one, which acts rigid member. All joints are made as free from backlash as pos and the spring, *K*, is provided to take up the residual slack. some of the latent-heat experiments at high pressures, a set of silver palladium disks each 0.1 mm in thickness and with 0.5 mm

e centers, was introduced between the valve stem and the seat vide more paths for vapor and thus cut down the sensitivity of alve to motions imparted to it by the observer.

nsiderable difficulty was experienced in the evolution of the le valves. The two described proved to be the most satisfactory veral which were tried.

2. CONTAINERS FOR WATER

e containers for the water, as shown at *WR* in Figure 11, are of 1.6 mm silver in cylindrical form with hemispherical ends. capacity is about 425 cm³. Those for use in transferring liquid rovided with reentrant silver tubes reaching nearly to the m. Each container is provided with an outlet tube of silver as indicated in the figure and leading to a diaphragm valve. body of this diaphragm valve terminates in the male half of a , threaded to fit any of the unions on the tempering coils. weight of each container and its valve is about 1,000 g.

3. PUMP-SPEED CONTROL

e speed of the circulating pump in the calorimeter is accurately olled to make the rate at which it supplies energy to the water ite and reproducible.

e long external drive shaft for this pump has squared ends h couple the pump positively to a liquid tachometer, rotating e same speed as the pump. The tachometer, of the well-known er type, is driven by a motor which draws its power from a olt storage battery. The impeller maintains a column of kerosene height which is determined by the speed. A column of mercury side tube off the kerosene column is maintained at a level which varies with the speed. In a manner similar to that of the mostat, this mercury column, by its motion, serves to make and k an electric circuit. As a result, more or less resistance is d in the armature circuit of the driving motor, in the direction ired to maintain a constant head of mercury. The kerosene mn furnishes a sensitive means for the direct observation of the p speed, which latter is maintained practically constant by the matic control.

o check the constancy of the pump rate, a revolution counter was d directly to the pump shaft. Observations with this counter nfrequent intervals showed that the pump rate is maintained tant at any desired value to about 0.1 per cent.

4. TIMING DEVICES

n the α and β experiments the time of electric heating and in the periments the time of withdrawal of vapor must be observed. the first of these there was constructed a double-pole double- w switch operated by a spring and a release which is actuated by lectric impulse from the standard clock. This automatic switch only opens or closes within less than 0.1 of a second, but also ires the same time interval for action in either direction. In ration it was used to switch the connection from a 30-volt storage tery to either the calorimeter heater or to a spill coil having nearly same resistance.

To provide for timing the flow in the γ experiments, the actuati mechanisms of the three previously described shut-off valves equipped with pulley wheels rigidly attached to the operating lev and rotating about the same axes as these levers. Cords firm attached to the wheels can be led in either direction around the whe and thence up to a spring. The spring is permitted to operate by release of a catch at a signal from the standard clock. The spri thus furnishes the power for opening or closing the valves at a chos time, either individually or in any desired combination. The ti required for complete opening or closing of a valve is less than of a second.

Signals from the standard clock are received only on the ex seconds, the fifty-ninth being omitted. The key in the clock circ is closed by the operator during the fifty-ninth second, so that t zero signal is used either for starting and stopping the power or diverting the vapor flow. The integral number of minutes involv in an observed process is observed on a watch.

5. PRESSURE-MEASURING INSTRUMENTS

Provision was made for observing pressure, and, although no me urements are included in this report, the installation will be describ A side tube from the outflow tube just after it emerges fr the vacuum space leads to a pressure capsule (*PC*, fig. which is also in the oil bath to avoid condensation. The press capsule is made of Monel metal with a 4-cm diameter sheet Mo diaphragm, *D*, 0.08 mm thick, stretched across the capsule. T diaphragm transmits the pressure from the vapor on one side to on the other. The diaphragm is allowed a displacement at the cen of only 0.25 mm from the mean position before coming against t solid supporting walls of the capsule. When the highest worki pressure is applied, no permanent deformation of the diaphragm w result. The diaphragm, however, is sufficiently flexible for a ve small pressure change to deflect it across the chamber. A measu ment of the opposing pressure when the diaphragm is balanc midway in the capsule will then give the pressure of the vapor. the Monel surfaces on the vapor side are silver plated to preve chemical action of the hot vapor with the metal. A 0.2 mm gold-wi ring was used to make the diaphragm gas tight in the capsule. Mo screws were used in addition to the Monel case and diaphragm that there would be no differential expansion of the parts which wou cause leaks or change in tension of the diaphragm. Oil is used transmit the pressure from the diaphragm in the capsule to a gau of the dead-weight type with piston rotating in oil.

6. ELECTRICAL MEASURING INSTRUMENTS

The electrical measurements comprise observations of thermome resistance, thermoelectromotive force, and electric power input.

The resistances of the thermometers are measured with a Muelle bridge built by O. Wolff. The bridge coils are immersed in a th mostated oil bath. A separate commutator switch permits the o servation of any chosen one of four thermometers. The bridge co

[6] Mueller, B. S. Sci. Paper No. 288.

re recalibrated whenever it was found desirable, by the method tlined by Mueller. A measuring current of 4.5 milliamperes was ed both in the calibration and in the measurements of temperature. galvanometer scale deflection of 1 mm corresponds to approxi- te 0.0001 ohm, or about 0.001° C., for the thermometers used.

The electromotive forces of the thermoelements, amounting in arly all cases to less than 20 μv are measured on a Wolff potentiom- r designed by F. Wenner. By comparison with another instru- nt which had been calibrated at the Bureau of Standards, the cor- tions to the indications of this instrument were found to be negli- le in the range in which it is used. When the temperature of the lorimeter is being observed, a scale deflection of 1 mm corresponds 0.002° C. or less.

The power input is measured on a Diesselhorst potentiometer, ilt by O. Wolff. It was calibrated at the Bureau of Standards fore, during, and after the experimental work and showed no changes more than 1 part in 30,000. The scale deflection was greater than mm per division on the last dial in the measurements on current d potential drop.

The standard cells to which the potentiometric measurements are ferred are Eppley unsaturated cadmium cells. They are kept in a rk-lined box and calibrated frequently against the standards aintained at this bureau. Two of these cells are used with the tentiometer for power measurement to guard against fortuitous anges in voltage between calibrations. Their electromotive forces, measured and used in this work, are expressed in international volts. his international volt is defined as 1/1.0183 of the voltage of the rmal Weston cell at 20° C.

The volt box ratio and the resistance of the 0.01-ohm manganin andard used in the measurements were verified at this bureau before, ring, and after the experiments and showed no changes of more an 1 part in 30,000.

7. WEIGHING INSTRUMENT

The balance used in the weighings is a 2 kg Troemner balance, ith a sensitivity of one scale division per milligram. Provision was ade for suspending the counterpoise and the containers for water a closed cabinet below the balance pans. All weighings are made the method of substitution. The weights are of brass, platinum ated, and calibrated at this bureau. Correction is made for buoy- cy of the air on the weights. In this method of weighing no correc- on for the air buoyancy on the water sample is necessary. Changes buoyancy are compensated for by making the volume of the counter- ise approximately the same as the volume of a container. The eights are made to the nearest milligram.

8. THERMOMETRIC STANDARDS

All temperatures used in this work are measured on the inter- ational centigrade scale [7] of 1927, which is defined, in the interval to 660° C., by assigning the temperatures 0°, 100°, and 444.60° C. the ice point, steam point, and sulphur boiling point, respectively, at the pressure of one standard atmosphere (760 mm mercury);

[7] Burgess, B. S. Jour. Research (RP22), p. 635; October, 1928.

and establishes other points by means of a standard resistance th
mometer of pure platinum, making use of a formula of the form

$$R_\theta = R_o(1 + A\theta + B\theta^2)$$

in which θ is temperature, R_o the resistance at the ice point, and
and B are constants found by calibration at the steam point and
sulphur boiling point.

Before starting the calorimetric measurements the resista
thermometers were calibrated directly at the ice, steam, and sulp
points as outlined above. Later on in the work it was found
pedient to calibrate the thermometers by comparison with a labo
tory standard. A standard resistance thermometer of the strain-f
type was inserted into a special copper receptacle which is in g
thermal contact with the copper reference block in the control ba
This strain-free thermometer is calibrated at the ice, steam, a
sulphur points directly, and the constants of the calorimetric spa
type thermometers are determined by direct comparison in posit
in the control bath. In this way it was possible by holding the b
at a constant temperature to make very accurate comparisons betwe
the strain-free thermometer and the calorimetric thermomete
However, the strain-free thermometer was not so well adapted
indicating the temperature of the upper reference block during
calorimetric experiments, and for this reason the calorimetric th
mometers were used in the actual experiments.

The thermoelements used in measuring the calorimeter temperatu
were calibrated in place against the resistance thermometers. T
accuracy of this calibration is of little importance because of t
extremely small values of the observed thermoelectromotive forc

9. PURIFICATION OF WATER

Dissolved gases are removed from the water samples used in t
experiments. In a specially designed still, ordinary distilled water
subjected to another distillation under a pressure of about 0.1 atm
phere. During this redistillation a pump is continually removing t
permanent gases, together with some water vapor from the condens
at such a rate that there is little opportunity for the permanent gas
to redissolve in the condensate. In special test experiments t
amount of residual gas remaining in the condensate was found to
less than one one-thousandth of the amount usually contained in d
tilled water. After a water sample is thus freed from dissolved gas
it is not allowed to come into contact with air again either before
during its use in the experiments, but is always kept and transfer
under its own vapor pressure.

V. DESCRIPTION OF MEASUREMENTS

The keynote in the description of the experiments is that an acc
rate account must be kept of each of three primary observed qua
tities, namely, the amount of fluid subjected to the process, t
change in state, and the amount of energy exchanged. The ener
account consists primarily of that which is added and measured el
trically, but includes also the energy added by the pump and t
energy exchanged by thermal leakage. In the following discussi
the method employed for the evaluation of all these factors will
described.

1. ACCOUNTING FOR MASS OF WATER

The mass of water which is subjected to a change in state enters as a direct factor in the reduction of the data. The results, therefore, can be no more reliable than the determinations of the masses. In addition, a quantitative account of the aggregate mass of the water involved in any set of experiments throws important light upon the reliability of the data derived from the experiments. Equality of the amount put into the total removed indicates that there has been no gain or loss of fluid through leaks and that there have been no accidental errors in the determination or recording of weights. In this work such a mass accounting has been carefully kept, and important correlations have resulted from it. From time to time water leaks from the calorimeter and air or oil leaks into the calorimeter have been indicated, located, and eliminated. When the mass accounts balance properly, the results assume an added degree of certainty.

The procedure employed in filling the calorimeter and in removing that water which remained after the completion of a series of experiments is the same for the α, β, and γ experiments. It will therefore be described here once for all.

A container having a reentrant tube is evacuated and filled with a charge of water from the still. The valve on the container is heated to a little above 100° C. to drive off external moisture, and the whole is cooled in a current of air, from a fan, to the temperature of the room. This treatment was found to bring the containers to a reproducible condition for weighing, and will be spoken of hereafter as conditioning.

The container and its charge of water are first weighed and then attached to the tempering coil at the bottom of the calorimeter. The calorimeter and coil are then evacuated through the vacuum valve, until a McLeod gauge in the system indicates a pressure of less than .001 mm. The system is then considered tight and sufficiently gas free.

The vacuum valve is then closed and the container valve opened. The water in the container is forced into the calorimeter by its own vapor pressure when heat is applied with a gas torch. Usually the entire charge is introduced, but the flow can be stopped after any chosen part has gone in if the container is suspended during the filling from one arm of a crude balance.

When the desired mass of liquid has flowed into the calorimeter, the lower calorimeter shut-off valve is closed, the tempering coil is surrounded with boiling water, and the container is immersed in cold, running water. Virtually all the water remaining in the lines is thus distilled back into the container. After a few minutes the container valve is closed and the coil is again evacuated, this time through the liquid air trap which has previously been evacuated and weighed. The vacuum valves and the valves on the trap are closed and the container and trap are detached, conditioned, and weighed. The change in weight of the container minus the weight of the water caught in the trap (always less than 1 mg, and therefore negligible when the operations are properly carried out) gives the mass of the water in the calorimeter system.

After a set of experiments in which part of the water sample may or may not have been removed, the water remaining in the calorimeter

is withdrawn into the container. This process is hastened by ha the calorimeter and tempering coil hot and the container cool. W as much liquid as will flow out has been collected in the conta its valve is closed and that which remains in the calorimeter is colle in the liquid air trap. The masses thus removed are weighe described above.

In the constant mass or α experiments the mass weighed equal to the mass removed if the operations have been prop performed. In the withdrawal, or β and γ, experiments the m of water removed as saturated liquid or vapor must be included i mass accounting.

2. HEAT-CAPACITY DETERMINATIONS

The measurements of the first type which determine the chan value of the quantity $H-L\frac{u}{u'-u}$, denoted by the symbol α, w with a few exceptions, taken in 10° intervals. The whole range f 0° to 270° C. was divided into three sections, 0° to 100°, 100° to 2 200° to 270°, each of which could generally be covered in a s day's work. Starting at the lowest temperature of one of the secti 0° C., for intsance, the initial temperature is observed. Then ele energy is added to heat the calorimeter and water approximately The temperature is again observed and energy added for ano period. There is thus obtained a series of observed temperatures tween which the added energy is measured. By keeping a contin account of the energy, including heat leak and pump energy, change in α from the initial starting point of the series to any stopp point can be determined independently of the intermediate inter A single series of measurements of this kind gives as a result the amo of energy, Q, added to change the temperature of the calorim and contents from any one to any other of the observed temperatu A second series carried out in a similar manner over the same inter of temperature but with a different mass of water in the system g as a result a second series of values of Q corresponding to these s temperature intervals. Two such series of measurements suffic determine a series of values for the changes in α and for the cha in another quantity which is designated as Z, over the tempera intervals covered. This quantity Z, as described more fully in paper on the analysis,[8] is a characteristic property of the calorim as used, and its value depends on the temperature but is indepen of the total amount of water in the system. Actually, in each ra of temperature several series were made in which the masses of w contained were chosen so as to give large differences in total h capacity. Reduction of the results of such a group as a whole the method of least squares yields a series of values of α, which property of saturated liquid water, and a series of values of Z, w is a property of the calorimeter as it was used. The individual va of α, corresponding to each experiment, can then be calculated purposes of comparison to show the degree of reproducibility of measurements of α.

In all the measurements of this type a tight-fitting cap seals calorimeter at A in Figure 11. The water samples are introdu

[8] See footnote 2, p. 412.

d removed as liquid through the connection at the bottom of the orimeter as previously described.

The shut-off valve in the water line is outside the boundary of the orimeter, and so a small part of the water introduced into the sys- is outside the calorimeter and does not enter into the thermal cess observed. This fact in no way affects the result because the thod of reducing the observations eliminates it as a quantity ependent of the amount of filling. Only minor differences, such, instance, as fortuitous changes in the temperature of the all emergent portion of the water sample, could affect the results. ese effects would appear as accidental errors in a large group of asurements.

The energy imparted by the pump during an experiment is taken o account in computing the results. The pump power is deter- ned by supplementary experiments in which no electric power is pplied and heat s is deter- ned, as will be scribed pres- ly.

In the heat-ca- city experi- nts it is not im- rtant that the mp power be own accurately. e method of re- ction by com- ing results of periments dif- ring only in nount of water mple used elimi- tes the pump ergy from the al result except r its variation om one experiment to another. Changes in this factor would enter accidental errors in a series. Experiment showed that no sys- matic difference in pump power resulted from the use of different nounts of water.

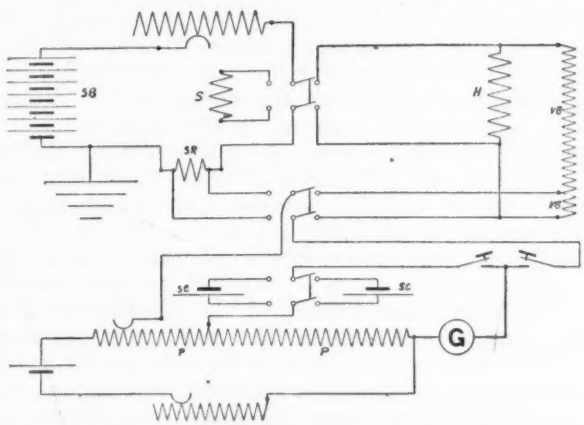


FIGURE 10.—*Wiring diagram for calorimeter heating power and its measurement*

H, calorimeter heater; *S*, spill coil; *SB*, storage battery; *SR*, standard resistance; *VB*, bolt box; *P*, potentiometer; *SC*, standard cells; *G*, galvanometer.

The group of measurements in the range 0° to 100° C. differed from ose in the other higher ranges in several respects. In the first ace, it was necessary to cool the calorimeter from the laboratory mperature down to the starting point of the series as a preliminary the experiments. At best this preliminary cooling was a slow ocess. On the other hand, the pressures in this range were low and e work was freer from leakage troubles incident to pressure. The easurements from 100° to 200° could be made more expeditiously, t difficulties incident to the higher temperatures and pressures were eater. Above 200° these difficulties increased, and other obstacles operation were encountered. These resulted in a greater percentage failures and necessitated occasional suspension of the observations r changes and repairs.

A determination of heat capacity in the range 0° to 100° will
described to illustrate the principal features of the determinatio
over any temperature range. The procedure is, in general,
follows:

A weighed sample of water is introduced into the calorimeter.
provide a medium for extracting heat from the calorimeter a
expedite the cooling down to the initial temperature of the seri
helium is introduced into the space between the calorimeter and
envelope to a pressure of about 10 cm of mercury. This gas w
used because of its relatively high thermal conductivity.

Carbon dioxide is used as the refrigerating medium both for cooli
the bath down and for holding it at the low temperature while t
calorimeter is being cooled. During this period of cooling the calori
eter the bath is held very near, but not below 0° C. because freezi
of the water in the lower tube must be avoided.

The automatic thermoregulator is used during this time to maint
a practically steady temperature of the bath. It operates by co
pensating the excess refrigeration with electric heating, automatica
regulated in the manner previously described.

When the calorimeter has cooled to the desired temperature, t
bath temperature is raised to the same value. The helium is th
pumped out of the envelope space, leaving the residual pressure le
than 0.001 mm of mercury. The automatic thermoregulation, t
pump speed, and the power supply which is to furnish heat to t
calorimeter are all finally adjusted. The mantle around the referen
block is lowered, and after a short wait for a steady state to be reach
the preliminaries are complete and the observations are begun.

The initial temperature of the calorimeter is measured by taki
simultaneous readings on the resistance thermometers and the em
of the five thermoelements on the calorimeter in series. Two observ
tions on each of the three thermometers are taken for a determinati
of a single temperature. Readings are begun two minutes previo
to the time chosen for switching on the power to the calorime
heater and are continued at 20-second intervals until the six temper
ture observations have been made. The order used in reading t
thermometers is not important, but was kept the same at the beginni
and end of each experiment.

The operator increases the energy supply to the bath a little bef
switching on the power to the calorimeter heater, so that the envelo
temperature and the calorimeter temperature will start to rise
nearly the same time and the same rate. On the chosen zero insta
the automatic switch is thrown and the current started in the cal
rimeter heater. The operator, guided by indications of the differe
tial thermoelements, keeps the power supply to the bath so adjust
that the rising temperatures of the calorimeter and envelope are ke
very nearly together.

At 1-minute intervals the small temperature differences as indicat
by the differential thermoelements are observed. The record
observes the current and potential drop in the heater on alterna
minutes.

The heating is continued for an integral number of minutes a
stopped on the zero of that minute when the temperature is neare
to 10°. By proper preliminary adjustment of the power supply t

al temperature is brought in nearly all cases to within less than ° of the chosen even temperature.

Just before the end of the heating period the operator decreases e power supply to the bath so that the bath temperature will not ceed the final temperature of the calorimeter. On the chosen stant the automatic switch is thrown and the current stopped in e calorimeter heater. As quickly as possible the bath temperature ntrol is shifted to the thermoregulator, and a few minutes are owed for the establishment of a steady state. During this interim, adings of the differential thermoelements are continued. Within seconds after the power is turned off, the calorimeter temperature s become uniform.

When the bath temperature has become steady, the temperature the calorimeter is observed as previously described. During the erim the power now on the spill is readjusted to take care of the ange in the heat capacity of the calorimeter and its contents over e next 10° interval. This makes it possible to stop at very nearly ° with an integral number of minutes of heating.

The final temperature of the first interval is the initial temperature the second interval. The experiments are continued in steps of 10° far as desired.

For temperatures of 60° and above, no refrigeration is required r the satisfactory regulation of the bath temperature.

3. LATENT-HEAT DETERMINATIONS

The measurements of the second type which determine the value the quantity $L+L\frac{u}{u'-u}$, denoted by the symbol γ, were carried out certain chosen temperatures at which the values of L, the heat of porization, were desired.

The process of evaporating and removing saturated vapor is a flow ocess, and in these experiments the instrument is used as a flow lorimeter with storage for the fluid sample. The experiments are rried out strictly as flow experiments proceeding at a steady state. was possible to perform them as successive determinations, immedi- ly following one another without disturbance of the steady con- ion. Sometimes as many as eight separate measurements were de in one series during a day's work.

The procedure for the measurement of latent heat is in general as follows:

A weighed charge of water is introduced into the calorimeter. hree containers are evacuated, conditioned, weighed, and attached the three vapor lines. The lines up to the shut-off valves are then acuated and the vacuum valves closed.

In the following discussion the three flow lines for vapor and the rresponding shut-off valves will be designated as Nos. 1, 2, and 3. his numbering is convenient for the description of the manipulation, t has no further significance. In the preliminary operations to tablish the steady state the receiver in position 1 is used, and it ll be spoken of as the spill. When in use each of the tempering ils at the top is immersed in boiling water and each of the receivers cold running water.

During the preliminary heating of the calorimeter and bath, the ut-off valve and the receiver valve in the spill line are open. This

prevents any leak past the throttle from causing pressure to build on the diaphragm of the valves in the vapor lines. The calorim pump is running during the heating up and its speed is adjuste the desired value.

When the temperature chosen for operation is reached by both calorimeter and the bath, and when the bath temperature is prop held there by the thermoregulator, the withdrawal of vapor ca begun.

The current for the calorimeter heater, previously adjusted to value to give the desired rate of evaporation, is then turned on. throttle is opened and gradually adjusted to the rate of flow w will maintain the calorimeter temperature constant and equal to practically constant temperature of the envelope. The flow the spill in line 1 is continued for about a half hour while the oper completes the adjustment of the throttle to bring the calorimeter steady temperature. This much time at least was allowed to in that any liquid which had lodged in the tubes could be swept out a steady state of flow of dry saturated vapor established.

Meanwhile the automatic throw mechanism for the shut-off va is adjusted so that No. 1 will close and No. 2 open at a chosen si from the standard clock. The valve on the receiver in line No. opened to allow passage of vapor when shut-off valve No. 2 open

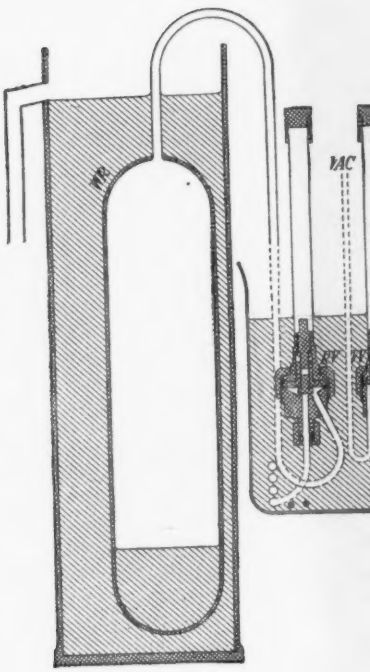
Before starting the measurements, a survey of the temperat existing at various points in the system is made to verify the existe of the steady state.

Six temperature observations are taken at times 10, 20, and seconds before and after the transfer of the flow from line 1 to lin For these observations simultaneous readings are taken of the res ance of a single thermometer and the emf of the five thermoeleme on the calorimeter in series.

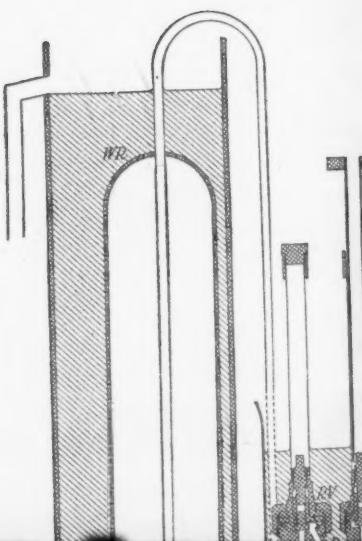
On the chosen minute the flow is shifted from line 1 to line Observations of the temperatures of the calorimeter and refere block are made on each succeeding minute, the operator maintain the calorimeter temperature as nearly constant as possible by adj ment of the throttle valve. Observations are made of current potential drop in the calorimeter heater on the alternate minu Meanwhile determinations are made of the mass of water which been removed, by weighing the spill and the residual water in lines which has been caught in the liquid air trap. A weig receiver is put in position 1 and the tempering coil evacuated. valve mechanism is reset to be ready for the transfer of the flow fr line 2 to line 3.

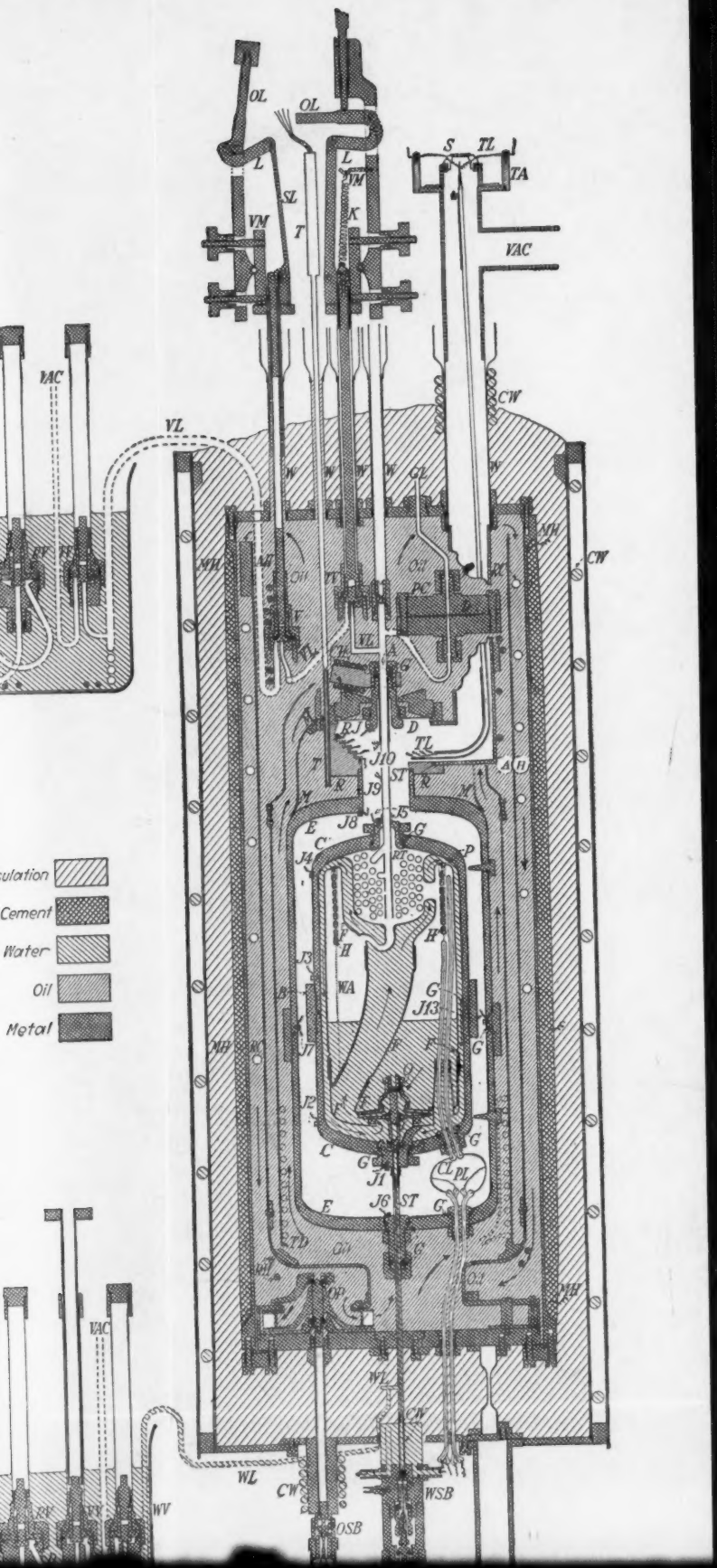
Water samples removed are usually about 30 g. The time o experiment is therefore determined by the rate at which the ene is supplied to the calorimeter. After the desired amount of w has been collected in position 2, temperatures are again measured before.

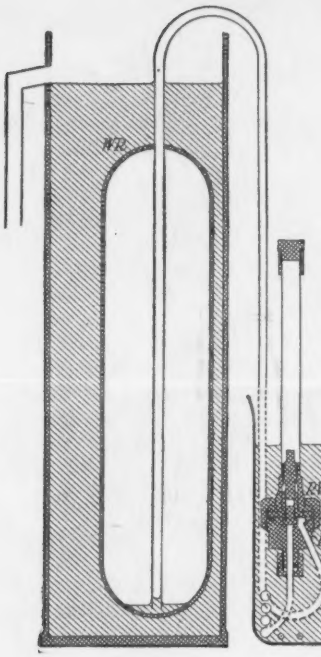
The above-described procedure is repeated as long as time or quantity of water in the calorimeter permits, each experiment c stituting an independent determination.



Insulation
Cement
Water
Oil
Metal




OL
OL
L
L
SL
VM
VM
K
T
S
TL
TA
VAC
VAC
CW
VL
W
GL
MH
MH
CW
Oil
PC
VL
RJ
D
TL
J10
ST
J9
J8
J5
G
C
J4
P
H
H
J3
WA
G
J13
MH
J7
F
G
J2
C
G
J1
CL
PL
E
J6
ST
G
TD
Oil
Oil
MH
VAC
WL
CW
WSB
WV
OSB
ulation
Cement
Water
Oil
Metal



FIGURE

(NOTE.—This is not a true

C, calorimeter shell (C
E, envelope shell (Cu-
B, threaded band (Mo
G, gold gaskets.
ST, support tubes (Ag-
(water and steam
I, pump impeller.
F, pump casing (Ag).
O, ball bearings (Ir all
P, water port.
H, calorimeter heater
WA, gauze apron (Ag)
CL, current lead (Au).
PL, potential lead (Au
PC, pressure capsule
GL, gage line.
WL, liquid water line
WSB, water stuffing b
WV, water valve.
WR, water receiver.
RV, receiver valve.
VAC, vacuum line.
VV, vacuum valve.
VL, vapor line.
V, shut-off valve.

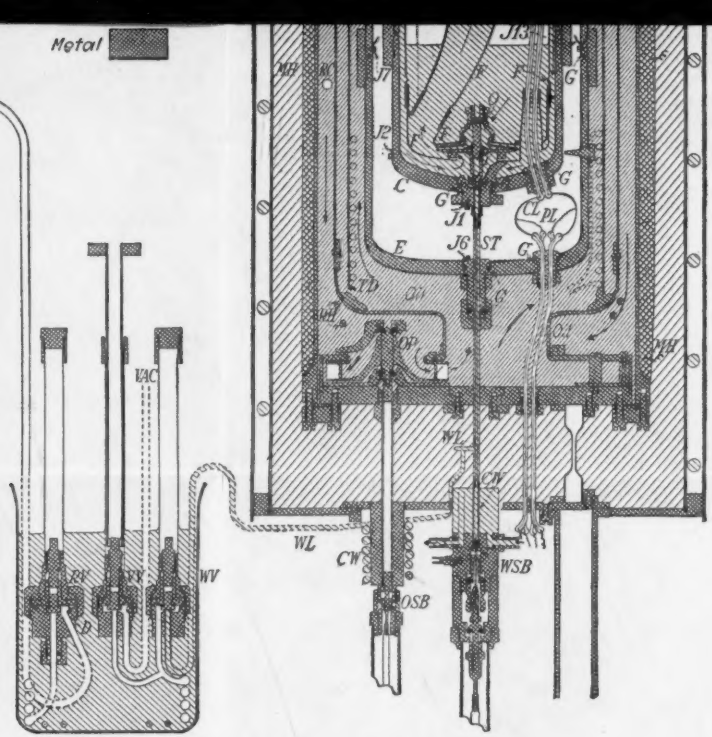


FIGURE 11.—*Section of assembled calorimeter*

not a true section but shows sections of important parts projected on a plane)

shell (Cu-Ni).
ell (Cu-Ni).
nd (Monel).
s.
ubes (Ag-Pd)
d steam outlets).
ler.
g (Ag).
s (Ir alloy).

heater (Ag).
ron (Ag).
ad (Au).
lead (Au).
apsule (Monel)

ter line (Ag).
uffing box.
lve.
eiver.
alve.
line.
valve.
.
ve.

TV, throttle valve.
VM, valve mechanism.
OL, operating lever.
SL, spring lever.
L, link.
K, backlash spring.
TD, thermoregulator dilatometer.
R, reference block (Cu).
D, diaphragm.
M, mantle.
*J*1, *J*2, * * *, principal junctions.
RJ, reference junctions.
TL, thermoelement leads (Au).
S, gas-tight insulating seal.
TA, anchorage for *TL* leads (Cu).
T, Pt resistance thermometer.
OIL, oil bath.
OP, oil pump.
OSB, oil stuffing box.
MH, main heater.
AH, auxiliary heater.
RH, regulating heater.
CH, central heater.
RC, refrigerating coil.
CW, cooling water.

118793°—30. (Face p. 438.)

4. EVAPORATION FACTOR

The α experiments yield values of the quantity $H - L\frac{u}{u'-u}$ and the γ experiments yield values of $L + L\frac{u}{u'-u}$. To determine the values of H and L from these quantities it is necessary to know the value of the quantity $L\frac{u}{u'-u}$, which has been designated as β. In the analysis[9] it is shown that this correction term β may be determined calorimetrically as the amount of energy which is supplied per gram of saturated liquid withdrawn at a constant temperature.

The procedure for a determination of β at a given temperature is as follows:

A weighed charge of water is introduced into the calorimeter. The temperatures of the calorimeter and the bath are brought to the value chosen for operation. The electric power on the spill is adjusted so that the proper rate of withdrawal of water will approximate a chosen value. The pump speed is adjusted and controlled as in the α and γ experiments.

A weighed container is attached to the lower tempering coil and the coil evacuated. The shut-off valve in the liquid line is now of the throttling type previously described, with arrangements for control by the operator at the instrument table.

The temperature of the calorimeter is measured as in the α experiments, and the power is similarly thrown on. As quickly as possible the operator opens the throttle for the liquid and adjusts it until the temperature of the calorimeter is constant and practically equal to the bath temperature. As in the α experiments, readings of the differential thermoelements and the power to the heater are recorded at the successive 1-minute intervals. At the chosen instant for stopping the experiment the power is cut off. The throttle is closed at such a time that the final temperature of the calorimeter is nearly the same as that of the bath. If the calorimeter is a little too hot, more liquid can be withdrawn until the desired state is reached. The final temperature is then measured as before. The water withdrawn is collected and weighed in the manner already described.

No provision was made for making more than a single β experiment at a time, and therefore it was necessary to measure only the time of electric heating and not the time of flow.

5. THERMAL LEAKAGE

When a difference of temperature exists between the calorimeter and its envelope, there is an accompanying transfer of heat by radiation, conduction, and convection. For small temperature differences the amount of energy transferred per unit time is proportional to this temperature difference.

In operation it is impossible to keep the temperatures of the calorimeter and its envelope identical at all times. The existing temperature difference can, however, be kept very small, and over a period of time can be so controlled that the integrated value is almost zero. In the measurements this ideal was approached as the operator gained experience.

[9] See footnote 2, p. 412.

To properly correct for the thermal leakage in those experiments where the temperature difference did not integrate to zero, a set of experiments was performed to determine the thermal-leakage coefficient. These experiments are performed under temperature conditions which are identical, as far as is possible, with those prevailing during the α, β, and γ experiments, except that the temperature difference between the calorimeter and its envelope is purposely much greater. The total amount of energy transferred under this exaggerated temperature difference, the value of the difference, and the time over which the difference exists are observed. No electrical energy is added to the calorimeter, and during most of the time of an experiment the pump is stopped. Thus practically all of the observed energy change is due to thermal leakage. Because the calorimeter was used both with the envelope space evacuated and filled with nitrogen, a set of heat-leak experiments under each of these conditions was necessary. These heat-leak experiments are carried out as follows:

The calorimeter is charged with about 250 g of water and its temperature and that of the bath are brought to the temperature chosen for operation. The initial temperature is observed with the pump running, and on the next minute the pump is stopped. The temperature of the bath is then raised or lowered until the envelope is either hotter or colder than the calorimeter by an amount corresponding to about 100 microvolts (two-thirds of a degree) on the differential or regulating thermoelements. At 1-minute intervals readings of this indication are recorded in microvolts over a period of from 30 minutes to one hour. At the end of this time the bath temperature is brought back to that of the calorimeter and on an integral minute the pump is started to insure uniformity of temperature throughout the calorimeter. The final temperature is then observed as before.

The pump is stopped during most of the time of the experiment so that the uncertainty in the determination of the energy supplied by the pump does not enter into the determination of the thermal leakage rate. Small corrections are made for the energy supplied by the pump during the short intervals at the beginning and end of the experiment.

The data obtained in such an experiment, when combined with the previously determined heat capacity of the calorimeter and its contents, yield the amount of heat transferred per microvolt-minute at the temperature of the experiment. In accordance with Newton's law of cooling, this coefficient or thermal-leakage rate can be used as a factor which, when multiplied by the resultant number of microvolt-minutes for any experiment at that temperature, gives directly the net heat exchange due to heat leak. At the higher temperatures, where a small difference in temperature corresponds to a much larger difference in vapor pressure, the bath was kept colder than the calorimeter in the heat-leak experiments. This insured against the direct transfer of heat from the bath to the calorimeter by active boiling in the lower support tube.

The heat-leak experiments, on account of the method in which they are performed, furnish an opportunity for the direct calibration of the thermoelements against the resistance thermometers. If the bath temperature is measured both before and after it is changed

multaneous indications of the five thermoelements on the calorimeter in series can be interpreted directly in terms of the thermometers, since the change in the calorimeter temperature in the short interval of time involved is small. Only the five series thermoelements were so calibrated, because the indications of the others need not be expressed in degrees.

6. PUMP ENERGY

The energy supplied to the calorimeter by the pump appears as a correction which must be applied to obtain the total energy added in the α, β and γ experiments. As previously shown, the knowledge of the true value of this pump energy is not of vital importance in the determinations of α, but it appears directly in the evaluation of β and γ, and must therefore be carefully determined.

The pump energy determinations are carried out as follows:

The calorimeter, containing a known mass of water, is brought, along with the bath, to the temperature chosen for the observation. The pump speed is regulated to the desired value. The initial temperature of the calorimeter is measured at a chosen time. At 1-minute intervals the indications of the differential thermoelements are recorded. The bath temperature is raised from time to time to reduce the integrated value of the temperature difference between calorimeter and envelope to virtually zero. After a period varying from 30 minutes to one hour the final temperature of the calorimeter is observed.

The data obtained from such an experiment, together with the previously determined heat capacity of the calorimeter and its contents, yield directly the rate at which energy is supplied to the calorimeter by the pump.

Similar experiments carried out with different quantities of water in the calorimeter showed no systematic variation in the pump energy rate with the mass of the water.

Experiments were performed with the pump running at various speeds, but throughout most of the work the speed employed was about 900 revolutions per minute.

VI. RESULTS OF MEASUREMENTS

1. ALPHA EXPERIMENTS

In the following record of the results of the measurements the experimental data have been assembled in the form of tables. An example of the record of a single determination of heat capacity of the calorimeter and its charge of water, over a 10° interval, is given in Table 1. The total time of experiment over which the heat-leak and pump-energy corrections are applied is the interval between the middle instants of the initial and final periods of temperature readings. The total heat-leak factor for this interval is the sum of the heat-leak indications at 1-minute periods during this time. This factor in microvolt-minutes multiplied by the heat-leak coefficient in joules per microvolt-minute gives the heat-leak correction in joules. Numerous determinations of the heat-leak coefficient were made, and the values observed have been assembled in the form of a chart. (Fig. 12.)

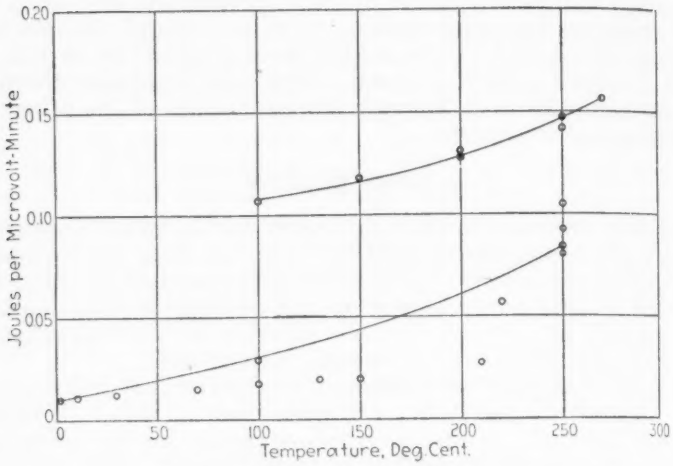


FIGURE 12.—*Heat-leak coefficient*

Lower curve with space evacuated; upper curve with nitrogen in space.

TABLE 1.—*Data sheet—Determination of heat capacity*

Experiment No. 193-U. January 26, 1929.

200° to 210° C.

Observers: N. S. O., H. F. S., and E. F. F.

Time	Thermometers		Thermo-elements		Electric power	
	Desig-nation	Bridge	t. e. 1–5	Regu-lating	I	E
		Ohms	*μv.*	*μv.*	*Amperes*	*Volts*
12.21.00	2 *n*	45.2890	9.0	2		
12.21.20	2 *r*	45.2939	8.8			
12.21.40	3 *r*	45.4794	8.8			
12.22.00	3 *n*	45.4735	8.5			
12.22.20	4 *n*	45.8176	8.6			
12.22	4 *r*	45.8143	8.7			
12.23				3		On.
12.24				0	1.9929	
12.25				2		20.195
12.26				2	1.9924	
12.27				1		20.195
12.28				−2	1.9920	
12.29				2		20.193
12.30				−5	1.9916	
12.31				−3		20.192
12.32				−1	1.9912	
12.33				0		20.193
12.34				−3	1.9909	
12.35				−2		Off 20.192
12.36				3		
12.37				2		
12.38				2		
12.39.00	2 *n*	46.2525	7.1			
12.39.20	2 *r*	46.2581	7.2			
12.39.40	3 *r*	46.4470	7.2			
12.40.00	3 *n*	46.4402	7.1			
12.40.20	4 *n*	46.7902	6.8			
12.40.40	4 *r*	46.7858	6.8			

Total heat-leak factor = +5 μv minutes. Total time of experiment 12.22 to 12.40=1,080 seconds. T time of electric heating, 12.23 to 12.35=720 seconds.

The correction for pump energy is computed as the product of t total time of the experiment by the pump power. The values of t pump power taken were those determined from time to time in spec

ank experiments for obtaining this quantity. Nearly 200 pump-ergy determinations were made throughout the experimental work, d the values observed have been assembled in the form of a chart. ig. 13.) In computing the results of the work on heat capacity the lues for pump power have been modified at various times in the ht of additional determinations. It has not been necessary to vise the earlier calculations on the basis of a uniform value for mp power, because this factor has so little effect on the final result. A partial reduction of the observations is given in Table 2. This cludes the computation of the initial and final temperatures of the lorimeter and the computation of the electric energy added. The lication of each of the three platinum resistance thermometers is

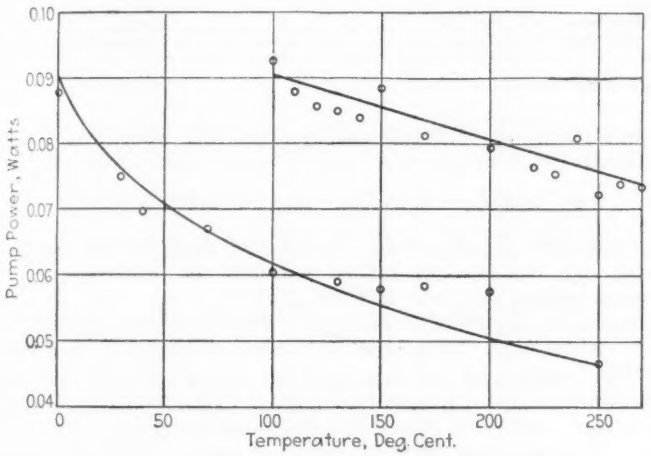


FIGURE 13.—*Pump power*

Lower curve with tachometer at 51 cm; upper curve with tachometer at 70 cm.

mputed separately. The mean of the three is then taken as the mperature of the reference block. The mean of the six readings of e five series thermoelements on the calorimeter, reduced to degrees, ves the difference in temperature between the reference block and e calorimeter. The observed temperature of the reference block nus this difference equals the calorimeter temperature at the middle tant of the series of temperature observations.

TABLE 2.—*Computation—determination of heat capacity*

Experiment No. 193-U. 200° to 210° C.

	Initial			Final		
rmometer No.	2	3	4	2	3	4
r 2	45.2914	45.4764	45.8159	46.2553	46.4436	46.7880
e correction	.0096	.0096	.0096	.0096	.0096	.0096
R_0	45.3010	45.4860	45.8255	46.2649	46.4532	46.7976
$(R_\theta - R_0)/(R_{100} - R_0)$	19.6930	19.7575	19.8716	20.6569	20.7247	20.8437
$\theta + (0.01\,\theta - 1)\,\delta$	197.090	197.095	197.064	206.737	206.744	206.704
ence block temperature	2.961	2.965	2.997	3.425	3.429	3.466
reference block temperature	200.051	200.060	200.061	210.162	210.173	210.170
t. e. 1–5 (microvolts)		200.057			210.168	
t. e. 1–5 (degrees)	8.73			7.03		
pera'ure of calorimeter		−.030			−.024	
		200.027			210.144	

Calculation of energy

Potentiometer	Current (amperes)		Volt
Mean reading	1.99183	Mean reading	
Pot. correction	.00020	Pot. correction	
Correction for std. 0.01 ohm	−.00010	Correction for volt-box factor	
Correction for volt-box current	−.00060		
Current I=	1.99133	Voltage E=	

Time of electric heating=t=	seconds	720	
Total electric energy=IEt=	joules		
Total time of experiment	seconds	1,080	
Pump power	watts	.0739	
Pump energy			
Total heat-leak factor	mv-min	5	
Heat-leak coefficient	joules/mv-min	.129	
Heat leak			
Entire energy added	joules		

The computation of temperature from the observed resistance the platinum thermometers is made by use of the Callendar formula

$$\theta = 100(R_\theta - R_0)/(R_{100} - R_0) + 0.01\theta(0.01\theta - 1)\delta.$$

The constants R_0, $R_{100} - R_0$, and δ are determined, as previou described, by calibration either directly or indirectly, using steam, and boiling sulphur as fixed points.

In computing the electric energy, corrections are applied for pote tiometer calibration, standard 0.01-ohm resistance, volt-box ra and for the fraction of the total measured current which is carried the volt box as a shunt across the heater. These corrections are add to the mean values of the potentiometer readings for current a voltage. The product of the corrected mean values of current a voltage, multiplied by the number of seconds of electric heating, gi the total energy added electrically. An approximation is involv in taking the means of the readings before taking the products, b in all these experiments the power was so nearly constant that ev in the extreme case this is less than 1 part in 100,000 and theref negligible.

The principal data from the entire group of experiments of this ty are given in Table 3. These experiments are arranged in groups, ea of which includes all those covering a certain temperature inter The masses given are corrected to the nearest milligram for error the weights. These masses are the amounts of water introduced i the system, including the portion filling the water line out to t shut-off valve. The initial and final temperatures and total elec energy are computed as described above.

TABLE 3.—*Principal data from a experimenta*

TABLE 3.—*Principal data from α experiments* $Q]_1^2 = M\alpha]_1^2 + Z]_1^2$. $\alpha]_1^2 = \left[\frac{H - L}{u' - u}\right]_1^2$

Experiment No.	Date	Mass of water M	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Time of electric heating	Total electric energy	Pump energy	Heat leak	Entire energy added Q	Energy for even temperature intervals $Q]_1^2$	$\alpha]_1^2$	Residual $\alpha]_1^2 - \alpha_m$
		g	°C.	°C.	*Seconds*	*Seconds*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*
35-A	June 10, 1927	487.107	1.402	10.285	1,320	540	25,427.3	116.4	2.6	25,546.2	28,769.8	41.982	−0.001
36-A	June 13, 1927	487.107	1.546	10.380	1,440	540	25,277.6	127.0	1.9	25,406.5	28,772.8	41.988	.005
37-A	June 16, 1927	487.107	1.504	10.273	2,580	1,020	24,981.5	228.0	3.2	25,212.8	28,763.2	41.968	−.015
42-A	July 11, 1927	326.833	1.627	8.987	1,380	480	16,091.9	120.6	1.6	16,214.1	22,032.0	41.953	−.030
45-A	July 14, 1927	326.833	2.508	9.209	1,380	420	14,645.2	119.8	1.5	14,766.5	22,039.0	41.975	−.008
46-A	July 16, 1927	326.833	1.323	9.265	1,380	480	17,374.3	120.0	1.6	17,495.7	22,033.8	41.959	−.024
49-A	July 22, 1927	493.054	1.602	9.818	1,320	480	23,727.8	116.1	1.3	23,845.2	29,033.6	42.010	.027
51-A	July 25, 1927	493.054	1.716	10.260	1,440	480	24,661.7	125.0	1.9	24,788.6	29,026.6	41.996	.012
57-A	Aug. 2, 1927	291.001	1.196	9.499	2,820	1,080	16,818.1	246.7	2.1	17,066.9	20,555.7	42.046	.063
58-A	Aug. 3, 1927	291.001	1.021	9.802	2,760	1,080	17,795.3	240.2	2.5	18,038.1	20,543.6	42.005	.022
59-A	Aug. 4, 1927	291.001	.908	9.880	2,580	1,080	18,204.3	225.4	3.5	18,433.2	20,546.7	42.015	.032
62-A	Aug. 9, 1927	366.801	.552	10.100	3,420	[1] 1,260	22,340.6	297.7	2.3	22,640.6	23,710.6	41.958	−.025
63-A	Aug. 10, 1927	366.801	1.029	10.083	2,340	[1] 1,080	21,256.0	203.3	1.6	21,460.9	23,702.8	41.937	−.046
Even-temperature interval 0°–10°. $Z]_0^{10} = 8{,}320.3$ Int. joules. Mean value of $\alpha]_0^{10} = \alpha_m = 41.9832$ Int. joules per g.													
35-B	June 10, 1927	487.107	10.284	20.210	1,500	598	28,394.3	120.5	3.8	28,518.6	28,731.0	41.799	−.003
36-B	June 13, 1927	487.107	10.380	20.447	1,440	600	28,808.9	115.7	1.8	28,926.3	28,732.6	41.802	.000
37-B	June 16, 1927	487.107	10.273	20.192	2,760	1,200	28,273.1	220.6	4.6	28,498.2	29,732.2	41.802	.000
38-B	June 17, 1927	487.107	9.955	19.653	2,940	1,200	27,628.9	236.2	3.3	27,868.5	28,736.1	41.810	.008
39-B	June 20, 1927	487.107	9.995	19.824	3,240	1,200	27,981.0	260.8	3.8	28,245.5	28,736.7	41.811	.009
42-B	July 11, 1927	326.833	9.136	20.203	1,740	660	24,235.8	140.2	1.6	24,377.6	22,025.8	41.781	−.021
46-B	July 16, 1927	326.833	9.265	19.212	1,440	600	21,788.4	116.0	1.6	21,906.0	22,024.7	41.778	−.024
49-B	July 22, 1927	493.054	9.817	20.445	1,560	660	30,677.7	124.4	1.7	30,803.8	28,979.0	41.798	−.004
51-B	July 25, 1927	493.054	10.259	19.688	1,620	600	27,193.5	127.9	3.1	27,324.5	28,980.9	41.802	.000
57-B	Aug. 2, 1927	291.001	9.500	19.147	1,500	600	19,691.1	120.2	1.3	19,812.6	20,538.7	41.816	.014
58-B	Aug. 3, 1927	291.001	9.802	19.923	1,920	600	20,637.9	153.9	1.0	20,792.8	20,542.2	41.828	.026
59-B	Aug. 4, 1927	291.001	9.879	20.015	1,440	600	20,703.7	113.8	1.7	20,819.2	20,539.5	41.818	.016
62-B	Aug. 9, 1927	366.801	10.100	20.625	1,620	[1] 780	24,818.4	129.0	1.0	24,948.4	23,699.9	41.793	−.009
63-B	Aug. 10, 1927	366.801	10.083	20.001	1,200	[1] 600	23,409.1	95.2	1.4	23,505.7	23,699.3	41.791	−.011
Even-temperature interval 10°–20°. $Z]_{10}^{20} = 8{,}370.5$ Int. joules. Mean value of $\alpha]_{10}^{20} = \alpha_m = 41.8016$ Int. joules per g.													

[1] Times were determined with a sidereal chronometer, and must be multiplied by 0.99735 to obtain mean solar seconds.

TABLE 3.—*Principal data from α experiments* $Q]_1^2 = M\alpha]_1^2 + Z]_1^2$. $\alpha]_1^2 = \left[H - L\frac{u}{u'-u}\right]_1^2$—Continued

Experiment No.	Date	Mass of water M	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Time of electric heating	Total electric energy	Pump energy	Heat leak	Entire energy added Q	Energy for even temperature intervals $Q]_1^2$	$\alpha]_1^2$	Residual $\alpha]_1^2 - \alpha_m$
		g	°C.	°C.	*Seconds*	*Seconds*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*
35–C	June 10, 1927	487.107	20.210	30.208	1,620	600	28,626.1	120.4	3.4	28,749.9	28,754.2	41.713	0.005
36–C	June 13, 1927	487.107	20.447	30.364	1,380	600	28,407.4	102.6	2.0	28,511.9	28,749.9	41.704	−.004
37–C	June 16, 1927	487.107	20.191	30.142	1,500	600	28,493.8	111.2	2.7	28,607.9	28,748.8	41.702	−.006
43–C	July 12, 1927	326.833	20.034	29.581	1,500	600	20,948.8	112.0	2.2	21,062.9	22,061.9	41.692	−.016
46–C	July 16, 1927	326.833	19.212	29.458	1,740	600	22,464.4	130.0	3.8	22,598.2	22,057.9	41.680	−.028
49–C	July 22, 1927	493.054	20.445	30.088	1,440	600	27,859.5	105.7	2.6	27,967.8	29,005.8	41.720	.012
51–C	July 25, 1927	493.054	19.688	29.507	1,380	600	28,368.2	101.7	2.8	28,472.7	28,998.2	41.705	−.003
53–C	July 27, 1927	493.054	19.809	29.487	1,800	600	27,929.1	131.9	3.2	28,064.2	29,002.7	41.714	.006
57–C	Aug. 2, 1927	291.001	19.147	29.899	1,380	660	22,014.6	103.0	1.4	22,119.0	20,572.5	41.707	−.001
58–C	Aug. 3, 1927	291.001	19.923	29.984	1,380	600	20,597.4	102.6	2.1	20,702.1	20,576.8	41.722	.014
59–C	Aug. 4, 1927	291.001	20.015	30.114	1,440	600	20,680.3	106.5	2.0	20,788.8	20,583.8	41.746	.038
62–C	Aug. 9, 1927	366.801	20.625	28.802	1,380	[1] 540	19,299.1	102.8	1.4	19,403.3	23,732.4	41.703	−.005
63–C	Aug. 10, 1927	366.801	20.001	29.889	1,200	[1] 600	23,376.3	88.9	1.4	23,466.6	23,731.4	41.700	−.008
Even-temperature interval 20°–30°. $Z]_{20}^{30} = 8{,}435.7$ Int. joules. Mean value of $\alpha]_{20}^{30} = \alpha_m = 41.7078$ Int. joules per g.													
35–D	June 10, 1927	487.107	30.209	40.169	1,380	600	28,580.2	97.3	3.1	28,680.6	28,973.7	41.703	.000
36–D	June 13, 1927	487.107	30.364	40.268	1,560	600	28,401.2	110.0	3.8	28,515.0	28,791.7	41.699	−.004
37–D	June 16, 1927	487.107	30.142	40.118	1,560	600	28,613.4	110.0	3.0	28,726.4	28,794.6	41.705	.002
43–D	July 12, 1927	326.833	29.850	39.633	1,560	600	21,507.6	109.7	1.7	21,619.0	22,100.6	41.675	−.028
46–D	July 16, 1927	326.833	29.458	39.576	1,380	600	22,263.8	96.5	1.4	22,361.7	22,103.6	41.684	−.019
49–D	July 22, 1927	493.054	30.089	39.914	1,380	600	28,440.1	96.8	2.3	28,539.2	29,047.4	41.715	.012
51–D	July 25, 1927	493.054	29.507	39.689	1,380	600	29,470.7	97.0	2.5	29,570.2	29,043.4	41.706	.003
53–D	July 27, 1927	493.054	29.487	39.523	1,500	600	29,037.4	105.5	3.4	29,146.3	29,044.9	41.709	.006
57–D	Aug. 2, 1927	291.001	29.899	40.553	1,380	600	21,868.9	96.7	1.7	21,967.3	20,616.8	41.707	.004
58–D	Aug. 3, 1927	291.001	29.984	40.000	1,140	600	20,571.9	79.9	1.9	20,653.7	20,619.7	41.717	.014
59–D	Aug. 4, 1927	291.001	30.114	40.002	1,200	600	20,316.1	83.8	1.3	20,401.2	20,632.5	41.761	.058
62–D	Aug. 9, 1927	366.801	28.802	40.356	1,380	[1] 780	27,368.1	96.7	1.6	27,466.4	23,774.0	41.696	−.007
63–D	Aug. 10, 1927	366.801	29.889	39.922	1,140	[1] 600	23,772.2	79.8	1.6	23,853.6	23,765.2	41.672	−.031
Even-temperature interval 30°–40°. $Z]_{30}^{40} = 8{,}480.0$ Int. joules. Mean value of $\alpha]_{30}^{40} = \alpha_m = 41.7032$ Int. joules per g.													
35–E	June 10, 1927	487.107	40.169	50.068	1,320	600	28,541.7	88.9	2.5	28,466.5	28,844.4	41.705	.007
36–E	June 13, 1927	487.107	40.268	50.136	1,320	600	28,374.2	93.9	2.8	28,704.4	28,857.7	41.691	−.013
37–E	June 16, 1927	487.107	40.118	50.072	1,380	600	28,697.7	104.4	3.0	22,889.4	22,153.5	41.685	−.019

35–E	June 10, 1927	487.107	40.169	50.098	1,320	600	28,341.7	89.9	2.8	28,434.4	28,340.6	41.708	.010
36–E	June 13, 1927	487.107	40.268	50.136	1,320	600	28,374.2	89.9	2.5	28,466.5	28,344.4	41.705	.007
37–E	June 16, 1927	487.107	40.118	50.072	1,380	600	28,607.7	93.9	2.8	28,704.4	28,837.7	41.691	−.007
43–E	July 12, 1927	326.833	39.633	49.965	1,560	600	22,782.0	104.4	3.0	22,889.4	22,153.5	41.685	−.013
49–E	July 22, 1927	493.054	39.914	49.861	1,440	600	28,830.6	97.3	1.7	28,929.6	29,084.1	41.688	−.010
51–E	July 25, 1927	493.054	39.689	50.055	1,440	600	30,055.0	97.5	2.2	30,154.7	29,093.6	41.707	.009
53–E	July 27, 1927	493.054	40.084	50.072	1,380	600	28,958.3	93.5	2.1	29,053.9	29,089.2	41.699	.001
57–E	Aug. 2, 1927	291.001	40.553	50.097	1,260	540	19,642.6	84.5	2.6	19,729.1	20,667.0	41.709	.011
58–E	Aug. 3, 1927	291.001	40.001	50.159	1,140	600	20,910.0	76.4	1.9	20,988.3	20,660.6	41.687	−.011
59–E	Aug. 4, 1927	291.001	40.002	49.867	1,440	600	20,296.6	96.1	2.1	20,394.8	20,673.2	41.730	.032
62–E	Aug. 9, 1927	366.801	40.356	50.450	1,200	[1] 660	23,932.6	80.1	1.0	24,013.7	23,821.9	41.691	−.007
63–E	Aug. 10, 1927	366.801	39.922	50.111	1,200	[1] 600	24,186.9	80.1	2.1	24,269.1	23,818.3	41.681	−.017

Even-temperature interval 40°–50°. $Z]_{40}^{50}$=8,529.7 Int. joules. Mean value of $\alpha]_{40}^{50}=\alpha_m$ =41.6981 Int. joules per g.

35–F	June 10, 1927	487.107	50.095	59.991	1,440	600	28,503.5	95.1	3.6	28,602.3	28,903.7	41.685	.002
36–F	June 13, 1927	487.107	50.136	60.052	1,560	600	28,549.3	103.1	4.5	28,656.9	28,900.0	41.677	−.006
37–F	June 16, 1927	487.107	50.072	60.070	1,440	600	28,804.7	95.0	3.6	28,903.3	28,909.3	41.696	.013
44–F	July 13, 1927	326.833	49.962	60.055	1,440	600	22,322.4	93.7	2.0	22,418.1	22,210.1	41.647	−.036
49–F	July 22, 1927	493.054	49.861	59.995	1,500	600	29,446.5	98.7	2.7	29,547.9	29,158.3	41.695	.012
51–F	July 25, 1927	493.054	50.055	60.173	1,500	600	29,391.5	98.7	3.1	29,493.3	29,147.2	41.676	−.007
53–F	July 27, 1927	493.054	50.072	59.908	1,380	600	28,574.7	90.7	3.4	28,668.8	29,148.7	41.679	−.004
57–F	Aug. 2, 1927	291.001	50.097	60.100	1,380	600	20,647.1	88.8	1.9	20,737.8	20,740.0	41.722	.039
58–F	Aug. 3, 1927	291.001	50.159	60.096	1,200	600	20,521.2	77.2	2.8	20,601.2	20,727.9	41.681	−.002
59–F	Aug. 4, 1927	291.001	49.867	59.855	1,380	600	20,618.1	88.6	2.8	20,709.5	20,734.2	41.703	.020
62–F	Aug. 9, 1927	366.801	50.450	59.584	1,320	[1] 600	21,731.3	84.9	1.0	21,817.2	23,884.6	41.673	−.010
63–F	Aug. 10, 1927	366.801	50.111	60.264	1,500	[1] 600	24,150.1	96.2	1.1	24,247.4	23,880.7	41.663	−.002

Even-temperature interval 50°–60°. $Z]_{50}^{60}$=8,598.6 Int. joules. Mean value of $\alpha]_{50}^{60}=\alpha_m$=41.6833 Int. joules per g.

35–G	June 10, 1927	487.107	59.991	69.962	1,260	600	28,798.7	81.0	2.9	28,882.6	28,967.7	41.690	.007
36–G	June 13, 1927	487.107	60.052	69.997	1,380	600	28,714.6	88.7	3.8	28,807.2	28,965.1	41.685	.002
47–G	June 16, 1927	487.107	60.070	70.096	1,680	600	28,921.8	107.8	4.2	29,033.9	28,958.9	41.672	−.011
34–G	July 13, 1927	326.833	60.055	70.368	1,560	600	22,887.6	97.8	2.2	22,987.6	22,278.1	41.666	−.017
49–G	July 22, 1927	493.054	59.995	70.327	1,380	600	30,094.3	88.3	1.7	30,134.3	29,214.1	41.687	.004
50–G	July 23, 1927	493.054	59.997	70.202	1,500	600	29,714.9	96.0	2.6	29,813.5	29,212.5	41.685	.002
51–G	July 25, 1927	493.054	60.173	70.093	1,440	600	28,888.6	90.8	2.2	28,981.6	29,212.3	41.685	.002
52–G	July 26, 1927	493.054	60.156	70.048	2,040	600	28,768.7	130.1	2.4	28,901.2	29,215.7	41.690	.007
53–G	July 27, 1927	493.054	59.908	69.821	1,350	600	28,869.6	86.4	2.0	28,958.0	29,209.0	41.677	−.006
57–G	Aug. 2, 1927	291.001	60.100	70.061	1,320	600	20,629.8	82.9	2.2	20,714.9	20,787.0	41.673	−.010
58–G	Aug. 3, 1927	291.001	60.096	69.990	1,140	600	20,498.6	71.5	1.6	20,571.7	20,791.6	41.689	.006
59–G	Aug. 4, 1927	291.001	59.855	70.135	1,260	600	21,299.3	78.9	1.5	21,379.7	20,798.2	41.711	.028
62–G	Aug. 9, 1927	366.801	59.584	69.592	1,380	[1] 660	23,875.1	86.4	2.0	23,963.5	23,947.5	41.678	−.005
63–G	Aug. 10, 1927	366.801	60.264	70.195	1,140	[1] 600	23,711.2	71.5	1.3	23,949.7	23,947.4	41.677	−.006

Even-temperature interval 60°–70°. $Z]_{60}^{70}$=8,660.2 Int. joules. Mean value of $\alpha]_{60}^{70}=\alpha_m$=41.6828 Int. joules per g.

[1] See footnote 1, p. 445.

TABLE 3.—*Principal data from α experiments* $Q]_1^2 = M\alpha]_1^2 + Z]_1^2$. $\alpha]_1^2 = \left[H - L\frac{u}{u'-u}\right]_1^2$—Continued

Experiment No.	Date	Mass of water M	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Time of electric heating	Total electric energy	Pump energy	Heat leak	Entire energy added Q	Energy for even temperature intervals $Q]_1^2$	$\alpha]_1^2$	Residual $\alpha]_1^2 - \alpha_m$
		g	°C.	°C.	*Seconds*	*Seconds*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*
35–H	June 10, 1927	487.107	69.962	80.078	1,320	600	29,281.6	82.6	3.2	29,367.4	29,030.1	41.677	−0.008
36–H	June 13, 1927	487.107	69.907	80.439	1,560	600	29,071.5	97.6	4.2	29,173.3	29,037.9	41.693	.008
37–H	June 16, 1927	487.107	70.096	80.201	1,440	600	29,248.8	90.0	3.2	29,342.0	29,034.0	41.685	.000
44–H	July 13, 1927	326.833	70.474	80.725	1,500	600	22,816.3	91.5	2.5	22,910.2	22,342.4	41.653	−.032
49–H	July 22, 1927	493.054	70.327	80.621	1,440	600	30,059.6	89.6	4.3	30,153.5	29,285.6	41.693	.008
50–H	July 23, 1927	493.054	70.202	80.363	1,440	600	29,665.7	89.8	1.9	29,757.4	29,280.5	41.683	−.002
52–H	July 26, 1927	493.054	70.048	79.885	1,440	600	28,717.5	89.7	2.0	28,809.2	29,281.0	41.684	−.001
53–H	July 27, 1927	493.054	69.821	80.169	1,350	600	30,216.3	84.3	1.8	30,302.4	29,282.3	41.686	.001
57–H	Aug. 2, 1927	291.001	70.061	79.982	1,380	600	20,610.7	84.4	1.9	20,697.0	20,861.5	41.693	.008
58–H	Aug. 3, 1927	291.001	69.990	80.016	1,260	600	20,834.2	77.0	1.7	20,912.9	20,858.0	41.681	−.004
59–H	Aug. 4, 1927	291.001	70.135	80.218	1,440	600	20,955.7	87.9	3.1	21,046.7	20,869.7	41.721	.036
62–H	Aug. 9, 1927	366.801	69.592	80.268	1,260	[1] 660	25,561.6	77.0	1.4	25,640.0	24,016.4	41.678	−.007
63–H	Aug. 10, 1927	366.801	70.195	80.087	1,140	[1] 600	23,686.3	69.6	1.1	23,757.0	24,015.3	41.675	−.010
Even-temperature interval 70°–80°. $Z]_{70}^{80} = 8{,}728.8$ Int. joules. Mean value of $\alpha]_{70}^{80} = \alpha_m = 41.6847$ Int. joules per g.													
35–I	June 10, 1927	487.107	80.078	90.269	1,380	600	29,580.7	84.2	3.2	29,668.2	29,111.9	41.673	.007
36–I	June 13, 1927	487.107	80.043	89.743	1,440	600	29,297.4	87.9	4.2	29,389.5	29,110.4	41.670	.004
37–I	June 16, 1927	487.107	80.201	90.333	1,500	600	29,402.7	91.5	2.9	29,497.3	29,111.7	41.673	.007
44–I	July 13, 1927	326.833	80.725	90.341	1,680	600	21,466.1	100.8	1.9	21,568.8	22,420.2	41.635	−.031
50–I	July 23, 1927	493.054	80.363	90.484	1,440	600	29,623.2	87.5	3.1	29,713.8	29,350.0	41.654	−.012
52–I	July 26, 1927	493.054	79.885	89.879	1,500	600	29,247.9	91.2	2.1	29,341.2	29,356.5	41.667	.001
53–I	July 27, 1927	493.054	80.169	90.355	1,320	600	29,825.0	80.3	2.6	29,907.9	29,357.5	41.669	.003
56–I	Aug. 1, 1927	291.001	79.908	89.551	1,440	600	20,098.1	86.6	2.3	20,187.0	20,936.7	41.671	.005
57–I	Aug. 2, 1927	291.001	79.981	90.006	1,380	600	20,910.8	83.1	1.3	20,995.2	20,941.0	41.678	.012
58–I	Aug. 3, 1927	291.001	80.016	89.981	1,140	600	20,793.9	68.6	1.1	20,863.6	20,934.6	41.656	−.010
59–I	Aug. 4, 1927	291.001	80.218	90.242	1,140	600	20,931.7	68.6	2.0	21,002.3	20,948.7	41.705	.039
62–I	Aug. 9, 1927	366.801	80.268	89.928	1,140	[1] 600	23,206.5	68.6	1.2	23,276.3	24,093.9	41.661	−.005
63–I	Aug. 10, 1927	366.801	80.086	89.938	1,080	[1] 600	23,665.6	64.9	1.4	23,731.9	24,088.1	41.645	−.021
Even-temperature interval 80°–90°. $Z]_{80}^{90} = 8{,}812.6$ Int. joules. Mean value of $\alpha]_{80}^{90} = \alpha_m = 41.6656$ Int. joules per g.													
35–J	June 10, 1927	487.107	90.269	100.480	1,560	600	29,722.6	93.0	4.2	29,819.9	29,198.6	41.689	−.001
36–J	June 13, 1927	487.107	90.139	100.239	1,800	600	29,388.1	107.4	4.1	29,499.6	29,205.7	41.704	−.014
37–J	June 16, 1927	487.107	90.333	100.495	1,440	600	29,582.9	85.4	3.1	29,671.4	29,195.1	41.682	−.036

[1] Heating period interrupted.

35–J	June 10, 1927	487.107	90.269	100.480	1,560	600	29,722.6	93.0	4.2	29,819.9	29,198.6	41.689	−.001	
36–J	June 13, 1927	487.107	90.139	100.239	1,800	600	29,388.1	107.4	4.1	29,499.6	29,295.7	41.704	−.014	
37–J	June 16, 1927	487.107	90.333	100.495	1,440	600	29,582.9	85.4	3.1	29,671.4	29,195.1	41.682	−.068	
44–J	July 13, 1927	326.833	90.341	100.073	1,440	600	21,814.7	85.2	2.1	21,901.9	22,500.2	41.638	−.052	
50–J	July 23, 1927	493.054	90.484	100.361	1,500	600	28,999.0	89.0	3.5	29,091.5	29,450.9	41.698	.008	
52–J	July 26, 1927	493.054	89.879	100.022	1,440	600	29,781.8	85.7	2.0	29,869.5	29,447.4	41.691	.001	
53–J	July 27, 1927	493.054	90.355	100.212	1,380	600	28,943.5	82.1	2.2	29,027.8	29,444.5	41.685	−.005	
56–J	Aug. 1, 1927	291.001	89.551	100.097	1,440	660	22,090.6	85.4	3.4	22,179.4	21,030.2	41.714	.024	
57–J	Aug. 2, 1927	291.001	90.007	100.164	1,320	600	21,279.8	78.1	1.8	21,359.7	21,029.1	41.710	.020	
58–J	Aug. 3, 1927	291.001	89.981	100.065	1,340	600	21,118.0	79.2	.8	21,198.0	21,023.0	41.689	−.001	
59–J	Aug. 4, 1927	291.001	90.242	100.217	1,170	660	20,910.2	69.3	1.0	20,980.5	21,028.8	41.709	.019	
62–J	Aug. 9, 1927	366.801	89.928	100.894	1,200	[1] 660	26,448.4	71.4	1.4	26,521.2	24,180.6	41.682	−.008	
63–J	Aug. 10, 1927	366.801	89.992	99.976	1,140	[1] 600	24,071.3	67.9	1.5	24,140.7	24,178.3	41.676	−.014	

Even-temperature interval 90°–100°. $Z]_{90}^{100}$=8,891.5 Int. joules. Mean value of $\alpha]_{90}^{100}=\alpha_m$=41.6896 Int. joules per g.

38–K	June 17, 1927	487.107	99.716	109.876	1,920	600	29,644.7	112.2	3.4	29,760.3	29,292.5	41.686	.008	
39–K	June 20, 1927	487.107	99.606	109.837	1,380	600	29,878.6	80.7	3.9	29,963.2	29,288.4	41.677	−.001	
52–K	July 26, 1927	493.054	100.126	110.223	1,320	600	29,749.8	76.8	3.5	29,830.1	29,536.8	41.678	.000	
53–K	July 27, 1927	493.054	100.212	109.985	1,440	600	28,775.3	83.7	2.0	28,861.0	29,534.2	41.673	−.005	
56–K	Aug. 1, 1927	291.001	100.097	109.936	1,440	600	20,694.7	84.7	2.2	20,781.6	21,123.2	41.704	.026	
60–K	Aug. 5, 1927	291.001	100.049	110.218	1,320	600	21,402.1	77.3	.8	21,480.2	21,119.3	41.691	.013	
87–K	Nov. 8, 1927	475.903	100.135	110.796	1,800	1,080	30,626.1	104.5	2.2	30,732.8	28,823.8	41.682	.004	
89–K	Nov. 10, 1927	475.903	100.104	110.293	1,800	1,200	29,267.8	104.4	.0	29,372.2	28,825.7	41.686	.008	
90–K	Nov. 11, 1927	475.903	100.066	110.309	1,740	1,200	29,427.5	101.0	.0	29,528.5	28,825.4	41.686	.008	
93–K	Nov. 15, 1927	263.730	100.103	110.107	1,740	1,200	19,881.9	100.9	−.5	19,982.2	19,973.2	41.656	−.022	
94–K	Nov. 16, 1927	263.730	100.030	110.044	1,740	1,200	19,911.6	100.9	−1.1	20,011.4	19,984.0	41.697	.019	
95–K	Nov. 25, 1927	267.764	100.217	110.046	1,740	1,200	19,700.8	101.0	−.4	19,801.4	20,144.5	41.669	−.009	
96–K	Nov. 26, 1927	267.764	100.095	110.044	1,800	1,200	19,938.7	104.6	−2.0	20,041.3	20,144.5	41.669	−.009	
97–K	Nov. 28, 1927	267.764	100.188	110.051	1,680	1,200	19,780.0	97.6	−2.4	19,875.2	20,150.3	41.690	.012	
112–K	Jan. 30, 1928	301.182	100.197	110.164	1,800	1,200	21,366.3	103.5	2.1	21,471.9	21,542.1	41.686	.008	
113–K	Jan. 31, 1928	410.025	100.032	110.331	1,800	1,260	26,747.7	109.8	.4	26,857.9	26,077.0	41.680	.002	
114–K	Feb. 1, 1928	410.025	99.974	110.452	1,860	1,260	27,208.5	103.5	1.3	27,313.3	26,066.3	41.654	−.024	
115–K	Feb. 6, 1928	419.333	100.049	110.178	2,100	1,260	26,669.4	128.3	1.4	26,799.1	26,457.4	41.662	−.016	

Even-temperature interval 100°–110°. $Z]_{100}^{110}$=8,987.2 Int. joules. Mean value of $\alpha]_{100}^{110}=\alpha_m$=41.6782 Int. joules per g.

[1] See footnote 1, p. 445.

TABLE 3.—*Principal data from α experiments* $Q]_1^2 = M\alpha]_1^2 + Z]_1^2$. $\alpha]_1^2 = \left[H - L\frac{u}{u'-u}\right]_1^2$—Continued

Experiment No.	Date	Mass of water M	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Time of electric heating	Total electric energy	Pump energy	Heat leak	Entire energy added Q	Energy for even temperature intervals $Q]_1^2$	$\alpha]_1^2$	Residual $\alpha]_1^2 - \alpha_m$
		g	°C.	°C.	*Seconds*	*Seconds*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*
38–L	June 17, 1927	487.107	109.876	120.052	1,500	600	29,817.4	85.9	3.6	29,906.9	29,389.0	41.676	−0.008
39–L	June 20, 1927	487.107	109.837	120.106	1,380	600	30,097.7	79.1	3.8	30,180.6	29,390.4	41.678	+.006
52–L	July 26, 1927	493.054	110.223	120.277	1,320	600	29,725.2	75.5	3.6	29,804.3	29,640.4	41.688	+.001
56–L	Aug. 1, 1927	291.001	109.936	119.903	1,380	600	21,073.2	80.5	2.8	21,156.5	21,226.5	41.711	.027
60–L	Aug. 5, 1927	291.001	110.218	120.156	1,380	600	21,013.1	80.4	2.1	21,095.6	21,224.1	41.703	.019
87–L	Nov. 8, 1927	475.903	110.796	120.192	1,800	1,080	27,081.0	102.8	2.1	27,185.9	28,927.0	41.686	.002
89–L	Nov. 10, 1927	475.903	110.293	120.441	1,980	1,200	29,247.3	113.1	.5	29,360.9	28,929.7	41.691	.007
90–L	Nov. 11, 1927	475.903	110.309	120.338	1,800	1,200	28,912.4	102.7	.5	29,015.6	28,928.8	41.690	.006
93–L	Nov. 15, 1927	263.730	110.107	120.073	2,300	1,200	19,867.5	131.3	+.4	19,998.4	20,065.5	41.622	+.062
95–L	Nov. 25, 1927	267.764	110.046	119.826	1,980	1,200	19,692.9	113.6	−.5	19,806.0	20,251.9	41.691	.007
96–L	Nov. 26, 1927	267.764	110.044	119.937	1,740	1,200	19,938.1	99.8	−2.5	20,035.4	20,249.9	41.684	.000
97–L	Nov. 28, 1927	267.764	110.051	119.867	1,800	1,200	19,775.7	103.2	−3.6	19,875.3	20,247.5	41.675	+.009
112–L	Jan. 30, 1928	301.182	110.164	119.951	1,920	1,200	21,073.4	114.7	1.8	21,189.9	21,650.2	41.708	.024
113–L	Jan. 31, 1928	410.025	110.331	119.623	1,620	1,140	24,232.0	96.8	1.4	24,330.2	26,183.7	41.691	.007
114–L	Feb. 1, 1928	410.025	110.452	120.030	1,740	1,140	24,967.8	103.9	.8	25,072.5	26,173.2	41.667	+.017
115–L	Feb. 6, 1928	419.333	110.178	120.033	1,740	1,200	26,077.4	103.9	1.8	26,183.1	26,565.8	41.679	+.005
Even-temperature interval 110°–120°					$Z]_{110}^{120}$=9,088.6 Int. joules.		Mean value of $\alpha]_{110}^{120} = \alpha_m$=41.6836 Int. joules per g						
38–M	June 17, 1927	487.107	120.053	130.284	2,760	600	30,029.9	155.3	5.1	30,190.4	29,507.1	41.672	+.005
39–M	June 20, 1927	487.107	120.106	130.389	1,320	600	30,269.9	74.3	3.8	30,347.0	29,508.4	41.674	+.003
52–M	July 26, 1927	493.054	120.277	130.077	1,320	600	29,089.1	74.1	3.6	29,166.8	29,754.5	41.671	+.006
56–M	Aug. 1, 1927	291.001	119.903	130.342	1,380	600	22,195.4	79.7	4.5	22,279.6	21,340.9	41.692	.015
60–M	Aug. 5, 1927	291.001	120.156	130.027	1,380	600	20,985.4	79.8	2.7	21,067.9	21,340.1	41.689	.012
87–M	Nov. 8, 1927	475.903	120.192	130.062	1,740	1,140	28,571.1	98.2	1.9	28,671.2	29,046.4	41.685	.008
89–M	Nov. 10, 1927	475.903	120.440	130.388	1,920	1,200	28,792.1	108.2	+.1	28,900.2	29,046.2	41.684	.007
90–M	Nov. 11, 1927	475.903	120.338	130.138	1,740	1,200	28,370.4	98.1	.2	28,468.7	29,047.9	41.688	.011
95–M	Nov. 25, 1927	267.764	119.826	129.792	1,800	1,200	20,194.2	101.7	+1.2	20,294.7	20,365.8	41.668	+.009
96–M	Nov. 26, 1927	267.764	119.937	129.894	1,680	1,200	20,185.0	94.8	−2.9	20,276.9	20,364.9	41.665	+.012
97–M	Nov. 28, 1927	267.764	119.867	129.957	1,620	1,200	20,462.4	91.4	−3.0	20,550.8	20,369.0	41.680	.003
112–M	Jan. 30, 1928	301.182	119.951	129.945	1,920	1,200	21,634.5	112.0	1.0	21,747.5	21,760.8	41.676	+.001
113–M	Jan. 31, 1928	410.025	119.623	129.890	1,800	1,200	26,889.1	105.0	1.2	26,995.3	26,297.6	41.678	.001
114–M	Feb. 1, 1928	410.025	120.029	130.054	1,680	1,200	26,289.7	98.0	.2	26,357.9	26,291.8	41.664	+.013
115–M	Feb. 6, 1928	419.333	120.033	130.053	1,740	1,260	26,633.2	101.5	1.3	26,736.0	26,681.6	41.669	−.008
Even-temperature interval 120°–130°.					$Z]_{120}^{130}$=9,208.6 Int. Joules.		Mean value of $\alpha]_{120}^{130} = \alpha_m$=41.6767 Int. joules per g.						
89–N	Nov. 10, 1927	475.903	130.388	139.984	1,860	1,200	27,895.6	104.2	+.9	27,998.9	29,178.5	41.703	.027
90–N	Nov. 11, 1927	475.903	130.137	139.936	2,700	1,200	28,433.5	150.4	1.7	28,585.6	29,170.2	41.697	−.004
	Nov. 11, 1927	475.903	130.338	139.964	1,860	1,200	20,153.8	103.7	−1.3	20,256.2	20,324.3	41.700	−.001

89–N	Nov. 10, 1927	475.903	130.388	139.984	1,860	1,200	27,893.4	150.4	1.7	28,585.6	29,170.2	41.697	−.004
90–N	Nov. 11, 1927	475.903	130.137	139.936	2,700	1,200	28,433.5	103.7	−1.3	20,256.2	20,324.3	41.700	−.001
93–N	Nov. 15, 1927	263.730	129.997	139.964	1,860	1,200	20,153.8	97.0	−1.3	20,488.4	20,493.7	41.704	.003
95–N	Nov. 25, 1927	267.764	129.793	139.792	1,740	1,200	20,392.7	97.0	−3.6	20,890.1	20,492.7	41.701	.000
96–N	Nov. 26, 1927	267.764	129.895	140.089	1,740	1,200	20,796.7	97.0	−1.6	20,557.1	20,493.8	41.705	.004
97–N	Nov. 28, 1927	267.764	129.957	139.988	1,740	1,200	20,461.7	106.3	2.3	22,030.0	21,887.6	41.705	.004
112–N	Jan. 30, 1928	301.182	129.945	140.009	1,860	1,200	21,921.4	120.0	1.6	26,757.2	26,423.3	41.696	−.005
113–N	Jan. 31, 1928	410.025	129.890	140.017	2,100	1,200	26,635.6	96.0	.8	26,324.8	26,417.9	41.683	−.018
114–N	Feb. 1, 1928	410.025	130.054	140.019	1,680	1,200	26,228.0	99.4	1.3	26,717.2	26,812.7	41.700	−.001
115–N	Feb. 6, 1928	419.333	130.053	140.017	1,740	1,200	26,616.5						

Even-temperature interval 130°–140°. $Z]_{130}^{140}$=9,326.7 Int. joules. Mean value of $\alpha]_{130}^{140}=\alpha_m$=41.7008 Int. joules per g.

87–O	Nov. 8, 1927	475.903	140.403	150.687	1,920	1,200	30,043.7	105.7	2.0	20,151.4	29,305.7	41.701	−.012
89–O	Nov. 10, 1927	475.903	139.984	149.949	1,980	1,200	29,103.2	109.0	−2.1	29,210.1	29,312.8	41.716	.003
90–O	Nov. 11, 1927	475.903	139.937	149.957	1,860	1,200	29,274.1	99.2	−.6	29,372.7	29,314.5	41.719	.006
93–O	Nov. 15, 1927	263.730	139.964	150.226	1,800	1,200	20,893.6	99.2	−2.2	20,990.6	20,452.5	41.680	−.033
95–O	Nov. 25, 1927	267.764	139.792	149.969	1,740	1,200	20,906.2	95.9	−2.6	20,999.5	20,633.6	41.728	.015
96–O	Nov. 26, 1927	267.764	140.089	150.219	1,980	1,200	20,789.2	109.2	−3.4	20,895.0	20,625.5	41.698	−.015
97–O	Nov. 28, 1927	267.764	139.988	150.068	1,800	1,200	20,698.9	99.2	−1.8	20,796.3	20,631.5	41.721	.008
112–O	Jan. 30, 1928	301.182	140.010	150.173	1,980	1,200	22,275.7	111.0	2.7	22,389.4	22,031.1	41.738	.025
113–O	Jan. 31, 1928	410.025	140.017	150.213	1,860	1,200	26,983.7	104.3	1.7	27,089.7	26,567.4	41.722	.009
114–O	Feb. 1, 1928	410.025	140.019	149.930	2,100	1,200	26,204.1	117.8	.9	26,322.8	26,559.3	41.703	−.010
115–O	Feb. 6, 1928	419.333	140.017	149.990	2,100	1,200	26,759.6	117.8	2.1	26,879.8	26,951.9	41.713	.000

Even-temperature interval 140°–150°. $Z]_{140}^{150}$=9,460.3 Int. joules. Mean value of $\alpha]_{140}^{150}=\alpha_m$=41.7127 Int. joules per g.

88–P	Nov. 9, 1927	475.903	150.712	160.406	1,920	1,140	28,458.7	104.5	2.3	28,565.5	29,459.1	41.699	−.004
89–P	Nov. 10, 1927	475.903	149.949	160.148	1,740	1,200	29,960.7	94.8	−1.6	30,053.9	29,466.3	41.714	.011
90–P	Nov. 11, 1927	475.903	149.957	160.362	1,860	1,200	30,556.0	101.4	−.4	30,657.0	29,461.4	41.704	.001
93–P	Nov. 15, 1927	263.730	150.226	159.779	1,740	1,140	19,595.1	94.8	−1.7	19,688.2	20,609.4	41.690	−.013
95–P	Nov. 25, 1927	267.764	149.970	160.073	1,740	1,200	20,893.5	94.8	−2.8	20,985.5	20,763.0	41.636	−.067
96–P	Nov. 26, 1927	267.764	150.219	159.963	1,800	1,200	20,159.8	98.0	−3.8	20,254.0	20,785.8	41.721	.018
97–P	Nov. 28, 1927	267.764	150.068	160.066	1,920	1,200	20,696.3	104.6	−2.8	20,798.1	20,795.4	41.757	.053
112–P	Jan. 30, 1928	301.182	150.173	160.256	1,860	1,200	22,263.3	102.0	2.7	22,368.0	22,180.1	41.721	.018
113–P	Jan. 31, 1928	410.025	150.212	160.292	1,920	1,200	26,824.0	105.2	3.3	26,932.5	26,714.0	41.704	.001
114–P	Feb. 1, 1928	410.025	149.930	159.959	1,920	1,200	26,679.6	105.2	−.7	26,784.1	26,706.4	41.685	−.018

Even-temperature interval 150°–160°. $Z]_{150}^{160}$=9,614.5 Int. joules. Mean value of $\alpha]_{150}^{160}=\alpha_m$=41.7027 Int. joules per g.

TABLE 3.—*Principal data from α experiments* $Q]_1^2 = M\alpha]_1^2 + Z]_1^2$. $\alpha]_1^2 = \left[H - L\frac{u}{u'-u}\right]_1^2$—Continued

Experiment No.	Date	Mass of water M	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Time of electric heating	Total electric energy	Pump energy	Heat leak	Entire energy added Q	Energy for even temperature intervals $Q]_1^2$	$\alpha]_1^2$	Residual $\alpha]_1^2 - \alpha_m$
		g	°C.	°C.	*Seconds*	*Seconds*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*
88–Q	Nov. 9, 1927	475.903	160.406	170.543	1,860	1,200	29,934.6	100.5	2.1	30,037.2	29,624.3	41.712	0.000
89–Q	Nov. 10, 1927	475.903	160.148	170.158	1,860	1,200	29,539.6	100.5	−2.0	29,638.1	29,623.7	41.711	−.001
90–Q	Nov. 11, 1927	475.903	160.362	170.390	1,740	1,200	29,622.0	94.0	−.3	29,715.7	29,627.2	41.719	.007
93–Q	Nov. 15, 1927	263.730	159.779	170.247	1,860	1,260	21,643.2	100.5	−.8	21,742.9	20,769.1	41.694	−.018
95–Q	Nov. 25, 1927	267.764	160.073	170.086	1,680	1,200	20,882.1	90.7	−1.5	20,971.3	20,950.2	41.742	.030
96–Q	Nov. 26, 1927	267.764	159.963	169.858	1,680	1,200	20,641.3	90.7	−4.0	20,728.0	20,945.6	41.725	.013
97–Q	Nov. 28, 1927	267.764	160.066	169.993	1,740	1,200	20,686.6	94.0	−4.1	20,776.5	20,933.6	41.680	−.032
112–Q	Jan. 30, 1928	301.182	160.256	170.258	1,920	1,200	22,247.7	103.2	2.1	22,353.0	22,341.1	41.728	.016
113–Q	Jan. 31, 1928	410.025	160.292	170.027	1,860	1,200	26,062.1	100.0	1.8	26,163.9	26,874.1	41.707	−.005
114–Q	Feb. 1, 1928	410.025	159.960	170.161	1,920	1,200	27,310.3	103.2	2.2	27,415.7	26,873.3	41.705	−.007
Even-temperature interval 160°–170°. $Z]_{160}^{170}$=9,773.3 Int. joules. Mean value of $\alpha]_{160}^{170}=\alpha_m$=41.7120 Int. joules per g.													
88–R	Nov. 9, 1927	475.903	170.543	180.113	1,980	1,140	28,412.7	106.0	2.4	28,521.1	29,798.0	41.691	−.010
89–R	Nov. 10, 1927	475.903	170.152	180.220	1,800	1,200	29,937.3	100.9	−4.0	30,034.2	29,813.2	41.723	.022
90–R	Nov. 11, 1927	475.903	170.389	180.213	1,800	1,200	29,189.0	96.3	.1	29,285.4	29,805.0	41.706	.005
93–R	Nov. 15, 1927	263.730	170.248	180.126	1,800	1,200	20,599.2	96.3	−.1	20,695.4	20,945.9	41.667	−.034
95–R	Nov. 25, 1927	267.764	170.086	180.007	1,740	1,200	20,872.7	93.2	−2.1	20,963.8	21,129.4	41.725	.024
96–R	Nov. 26, 1927	267.764	169.859	179.789	1,980	1,200	20,919.0	106.0	−4.1	21,020.9	21,128.8	41.722	.021
97–R	Nov. 28, 1927	267.764	169.993	180.424	1,800	1,260	21,944.9	96.3	−5.0	22,036.2	21,122.2	41.698	−.003
112–R	Jan. 30, 1928	301.182	170.259	180.053	1,800	1,200	21,961.0	95.0	2.4	22,058.4	22,519.1	41.709	.008
113–R	Jan. 31, 1928	410.025	170.027	179.951	1,980	1,200	26,742.4	104.9	.5	26,847.8	27,052.5	41.694	−.007
114–R	Feb. 1, 1928	410.025	170.161	180.245	1,800	1,200	27,179.8	95.3	1.8	27,276.9	27,045.7	41.677	−.024
Even-temperature interval 170°–180°. $Z]_{170}^{180}$=9,957.1 Int. joules. Mean value of $\alpha]_{170}^{180}=\alpha_m$=41.7009 Int. joules per g.													
88–S	Nov. 9, 1927	475.903	180.113	190.113	1,980	1,200	29,884.1	105.2	.7	29,990.0	29,988.4	41.660	.002
89–S	Nov. 10, 1927	475.903	180.225	190.223	1,680	1,200	29,912.0	89.2	−4.5	29,996.7	29,997.7	41.680	.022
90–S	Nov. 11, 1927	475.903	180.213	190.040	1,680	1,200	29,377.6	89.3	−.6	29,466.3	29,983.1	41.649	−.009
93–S	Nov. 15, 1927	263.730	180.126	189.651	1,800	1,140	20,040.2	95.7	−2.4	20,133.5	21,142.4	41.634	−.024
95–S	Nov. 25, 1927	267.764	180.007	189.949	1,800	1,200	21,109.9	95.6	−3.1	21,202.4	21,326.3	41.693	.035
96–S	Nov. 26, 1927	267.764	179.789	189.870	1,800	1,200	21,352.7	95.6	−3.9	21,444.4	21,319.6	41.668	.010
97–S	Nov. 28, 1927	267.764	180.424	189.889	1,680	1,140	20,095.1	89.2	−5.5	20,178.8	21,315.9	41.654	−.004
112–S	Jan. 30, 1928	301.182	180.053	189.885	1,800	1,200	22,228.2	95.5	.3	22,325.0	22,796.9	41.651	−.007
113–S	Jan. 31, 1928	410.025	179.952	189.894	1,800	1,200	26,734.6	96.5	.7	26,831.8	27,298.4	41.646	−.012
114–S	Feb. 1, 1928	410.025	180.245	189.753	1,800	1,140	25,798.2	90.6	1.6	25,897.0	27,298.3	41.646	−.012
89–T	Nov. 10, 1927	475.903	190.040	200.129	1,740	1,200	30,388.6	91.7	−1.9	30,478.4	30,208.7	41.681	.020
90–T	Nov. 11, 1927	475.903	190.040	200.129	1,740	1,200	22,132.1	98.0	−2.7	22,227.4	21,357.3	41.651	−.001
93–T	Nov. 15, 1927	263.730	189.651	200.059	1,860	1,200	21,254.3	98.0	−3.1	21,449.2	21,535.9	41.691	.039

90–T	Nov. 11, 1927	475.903	190.040	200.129	1,740	1,200	30,388.6	91.7	−1.9	30,478.4	30,208.7	41.681	.025
93–T	Nov. 15, 1927	263.730	189.651	200.059	1,860	1,260	22,132.1	98.0	−2.7	22,227.4	21,357.3	41.651	−.001
95–T	Nov. 25, 1927	267.764	189.949	199.910	1,860	1,200	21,354.3	98.0	−3.1	21,449.2	21,535.9	41.691	.039
96–T	Nov. 26, 1927	267.764	189.870	200.046	1,800	1,200	21,814.9	94.8	−5.9	21,903.8	21,523.3	41.644	−.008
97–T	Nov. 28, 1927	267.764	189.889	200.144	1,680	1,200	21,987.7	88.5	−4.7	22,071.5	21,531.3	41.674	.022
112–T	Jan. 30, 1928	301.182	189.885	199.763	1,860	1,200	22,529.8	94.8	3.2	22,627.8	22,909.8	41.627	−.025
113–T	Jan. 31, 1928	410.025	189.804	199.744	1,980	1,200	27,167.3	101.1	2.1	27,270.5	27,436.9	41.618	−.034
114–T	Feb. 1, 1928	410.025	189.755	199.677	1,860	1,200	27,126.8	94.8	1.7	27,223.3	27,440.4	41.626	−.026

Even-temperature interval 190°–200°. $Z]_{190}^{200}$=10,372.7 Int. joules. Mean value of $\alpha]_{190}^{200}=\alpha_m$=41.6514 Int. joules per g.

88–U	Nov. 9, 1927	475.903	200.327	210.173	1,860	1,200	29,858.4	97.3	−3.3	29,952.4	30,414.3	41.576	0.011
89–U	Nov. 10, 1927	475.903	200.150	210.146	1,740	1,200	30,312.9	91.0	−5.1	30,398.8	30,406.1	41.558	−.007
90–U	Nov. 11, 1927	475.903	200.129	210.145	1,800	1,200	30,367.6	94.1	−2.1	30,459.6	30,408.1	41.563	−.002
92–U	Nov. 14, 1927	263.730	200.530	210.347	1,800	1,200	21,122.8	94.1	−2.9	21,214.0	21,599.4	41.600	.035
93–U	Nov. 15, 1927	263.730	200.060	210.002	1,800	1,200	21,380.0	94.1	−3.0	21,471.1	21,595.4	41.585	.020
95–U	Nov. 25, 1927	267.764	199.910	209.991	1,680	1,200	21,851.6	87.8	−5.4	21,934.0	21,757.7	41.564	−.001
96–U	Nov. 26, 1927	267.764	200.046	209.954	1,740	1,200	21,467.8	90.9	−4.9	21,553.8	21,755.5	41.556	−.009
97–U	Nov. 28, 1927	267.764	200.145	210.079	1,680	1,200	21,403.3	87.8	−5.7	21,485.4	21,746.4	41.522	−.043

Group I, interval 200°–210°. $Z]_{200}^{210}$=10,628.3 Int. joules. Weight 1 to 5

173–U	Dec. 17, 1928	292.871	200.641	210.265	1,440	720	22,483.2	109.2	.0	22,592.4	23,464	41.490	−.013
174–U	Dec. 18, 1928	408.332	200.143	209.898	1,260	720	27,453.0	95.5	3.1	27,551.6	28,243	41.462	−.041
175–U	Dec. 19, 1928	414.265	200.153	210.104	1,320	720	28,250.3	100.1	−.9	28,349.5	28,486	41.455	−.048
176–U	Dec. 20, 1928	279.315	200.076	212.371	1,200	720	28,100.7	91.0	2.3	28,194.0	22,900	41.484	−.019
177–U	Dec. 21, 1928	413.267	200.147	210.167	1,320	720	28,430.4	100.1	1.5	28,532.0	28,472	41.521	.018
178–U	Dec. 26, 1928	288.124	200.157	209.947	1,140	720	22,690.9	86.4	−1.0	22,776.3	23,264	41.479	−.024
179–U	Dec. 27, 1928	415.134	200.092	210.123	1,500	720	28,512.2	113.7	1.0	28,626.9	28,537	41.491	−.012
181–U	Dec. 29, 1928	419.612	200.173	209.923	1,140	720	27,922.1	86.4	−.4	28,008.1	28,725	41.496	−.007
183–U	Jan. 2, 1929	285.531	200.187	209.956	1,240	720	22,513.7	94.0	3.0	22,610.7	23,144	41.436	−.067
184–U	Jan. 3, 1929	286.319	200.150	210.187	1,080	720	23,200.7	81.9	−.3	23,282.3	23,192	41.489	−.014
189–U	Jan. 22, 1929	420.292	200.137	210.344	1,140	720	29,293.2	63.0	1.7	29,357.9	28,757	41.505	.002
190–U	Jan. 23, 1929	277.212	200.207	210.231	1,260	720	22,819.9	69.7	1.8	22,891.4	22,832	41.554	.051
191–U	Jan. 24, 1929	278.960	200.317	210.323	1,080	720	22,826.4	82.0	.1	22,908.5	22,888	41.494	−.009
193–U	Jan. 26, 1929	419.181	200.027	210.144	1,080	720	28,964.8	82.0	.8	29,047.6	28,716	41.517	.014
195–U	Jan. 31, 1929	421.532	199.989	210.035	1,080	720	28,844.0	82.8	1.9	28,928.7	28,796	41.475	−.028

Group II, interval 200°–210°. $Z]_{200}^{210}$=11,312.8 Int. joules. Weight 5 to 1

Even-temperature interval 200°–210°. Mean value of $\alpha]_{200}^{210}=\alpha_m$=41.5026 Int. joules per g.

TABLE 3.—*Principal data from α experiments* $Q]_1^2 = M\alpha]_1^2 + Z]_1^2$. $\alpha]_1^2 = \left[H - L\frac{u}{u'-u}\right]_1^2$—Continued

Experiment No.	Date	Mass of water M	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Time of electric heating	Total electric energy	Pump energy	Heat leak	Entire energy added Q	Energy for even temperature intervals $Q]_1^2$	$\alpha]_1^2$	Residual $\alpha]_1^2 - \alpha_m$
		g	°C.	°C.	*Seconds*	*Seconds*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*
173–V	Dec. 17, 1928	292.871	210.265	220.213	1,200	720	23,493.2	89.6	0.7	23,585.5	23,701	41.406	0.014
174–V	Dec. 18, 1928	408.332	209.898	219.874	1,200	720	28,312.3	89.6	.1	28,402.0	28,473	41.383	−.008
175–V	Dec. 19, 1928	414.265	210.104	220.110	1,140	720	28,655.4	85.1	−2.5	28,738.0	28,718	41.382	−.009
177–V	Dec. 21, 1928	413.267	210.167	220.239	1,200	720	28,795.3	89.6	2.0	28,886.9	28,675	41.378	−.013
178–V	Dec. 26, 1928	288.124	209.947	219.928	1,200	720	23,369.9	89.6	−1.2	23,458.3	23,504	41.403	.012
179–V	Dec. 27, 1928	415.134	210.123	220.153	1,140	720	28,763.9	85.1	−3.5	28,845.5	28,755	41.385	−.006
181–V	Dec. 29, 1928	419.612	209.923	220.051	1,200	720	29,235.1	89.6	−2.0	29,322.7	28,953	41.415	.024
183–V	Jan. 2 1929	285.531	209.956	219.918	1,200	720	23,202.1	89.6	1.2	23,292.9	23,384	41.359	−.032
184–V	Jan. 3, 1929	286.319	210.187	220.189	1,080	720	23,356.7	80.6	−.7	23,436.6	23,428	41.399	.008
189–V	Jan. 22, 1929	420.292	210.344	220.417	1,200	720	29,141.5	65.4	2.7	29,209.6	28,989	41.434	.043
190–V	Jan. 23, 1929	277.212	210.231	220.137	1,140	720	22,778.1	62.2	1.5	22,841.8	23,054	41.409	.018
191–V	Jan. 24, 1929	278.960	210.323	220.222	1,200	720	22,798.2	89.7	.5	22,888.4	23,115	41.369	−.022
192–V	Jan. 25, 1929	419.602	210.339	220.278	1,260	720	28,670.7	94.2	1.2	28,766.1	28,935	41.373	−.018
193–V	Jan. 26, 1929	419.181	210.144	219.963	1,080	720	28,318.4	80.7	.5	28,399.6	28,916	41.369	−.022
195–V	Jan. 31, 1929	421.532	210.035	220.048	1,140	720	28,973.2	86.5	3.3	29,063.0	29,024	41.395	.004
	Even-temperature interval 210°–220°. $Z]_{210}^{220} = 11{,}574.8$ Int. joules. Mean value of $\alpha]_{210}^{220} = \alpha_m = 41.3908$ Int. joules per g.												
173–W	Dec. 17, 1928	292.871	220.213	230.171	1,200	720	23,775.0	88.0	−.8	23,862.2	23,957	41.355	.017
174–W	Dec. 18, 1928	408.332	219.874	230.201	1,260	720	29,562.2	92.4	.3	29,654.9	28,715	41.313	−.025
175–W	Dec. 19, 1928	414.265	222.371	230.407	1,020	600	23,221.6	74.8	−2.4	23,294.0	28,954	41.299	−.039
176–W	Dec. 20, 1928	279.315	220.264	229.968	1,140	720	22,623.9	83.6	−6.5	22,701.0	23,390	41.332	−.006
177–W	Dec. 21, 1928	413.267	220.239	230.305	1,140	720	29,054.7	83.6	−.5	29,137.8	28,941	41.367	.029
178–W	Dec. 26, 1928	288.124	219.928	230.140	1,200	720	24,176.4	88.0	−1.0	24,263.4	23,759	41.349	.011
179–W	Dec. 27, 1928	415.134	220.153	230.264	1,140	720	29,249.2	83.6	−2.2	29,330.6	29,004	41.333	−.005
181–W	Dec. 29, 1928	419.612	220.051	230.114	1,140	720	29,307.0	83.6	1.6	29,392.2	29,200	41.359	.021
183–W	Jan. 2, 1929	285.531	219.918	230.993	1,320	780	26,093.7	96.8	−3.8	26,186.7	23,632	41.280	−.058
184–W	Jan. 3, 1929	286.319	220.189	230.244	1,260	720	23,730.0	92.4	−.1	23,822.3	23,686	41.355	.017
189–W	Jan. 22, 1929	420.292	220.417	230.316	1,080	720	28,885.6	57.7	1.2	28,944.5	29,230	41.363	.025
190–W	Jan. 23, 1929	277.212	220.137	230.131	1,140	720	23,238.9	60.9	.8	23,300.6	41.364	41.364	.026
191–W	Jan. 24, 1929	278.960	220.222	230.182	1,140	720	23,205.3	83.6	−.5	23,288.4	23,376	41.334	−.004
192–W	Jan. 25, 1929	419.181	219.963	229.940	1,140	720	28,915.5	83.6	1.4	29,100.5	29,170	41.330	−.008
193–W	Jan. 26, 1929	421.532	220.048	229.960	1,080	720	28,934.3	79.2	.5	29,014.0	29,272	41.341	−.008
195–W	Jan. 31, 1929	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
173–X	Dec. 17, 1928	292.871	230.171	240.112	1,200	720	29,087.1	82.1	.6	29,169.2	28,986	41.282	−.020
174–X	Dec. 18, 1928	408.332	230.201	240.262	1,140	720	28,663.1	90.7	−1.5	28,752.3	29,226	41.282	−.020
175–X	Dec. 19, 1928	414.265	230.407	240.242	1,260	720	23,304.6	77.8	.6	23,383.0	23,665	41.318	−.015
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

173—X	Dec. 17, 1928	292.871	240.112	250.217	1,200	720	24,688.6	85.0	−.7	24,772.9	24,511	41.245	.003
174—X	Dec. 18, 1928	408.332	240.262	250.209	1,140	720	29,030.4	80.7	−3.3	29,107.8	29,257	41.205	−.037
175—X	Dec. 19, 1928	414.265	240.242	250.142	1,140	720	29,147.9	80.7	−3.6	29,225.0	29,515	41.238	−.004
176—X	Dec. 20, 1928	279.315	239.850	249.857	1,140	720	23,886.7	80.8	−.6	23,966.9	23,955	41.256	.014
177—X	Dec. 21, 1928	413.267	240.364	250.363	1,080	720	29,405.1	76.5	−1.5	29,480.1	29,472	41.234	−.008
178—X	Dec. 26, 1928	288.124	240.229	250.289	1,200	720	24,379.1	85.0	−1.6	24,462.5	24,308	41.220	−.022
179—X	Dec. 27, 1928	415.134	240.361	250.359	1,380	720	29,446.7	97.7	−2.2	29,542.2	29,537	41.205	−.037
181—X	Dec. 29, 1928	419.612	240.268	250.295	1,080	720	29,769.5	76.5	−1.4	29,844.6	29,757	41.289	.047
183—X	Jan. 2, 1929	285.531	240.422	250.441	1,200	720	24,166.5	85.0	−.1	24,251.4	24,192	41.188	−.054
184—X	Jan. 3, 1929	286.319	240.245	250.234	1,140	720	24,143.0	80.7	−1.0	24,222.7	24,242	41.249	.007
189—X	Jan. 22, 1929	420.292	240.120	249.914	1,020	720	29,116.2	52.7	.7	29,169.6	29,783	41.284	.042
190—X	Jan. 23, 1929	277.212	240.215	250.225	1,140	720	23,852.5	58.9	.4	23,911.8	23,881	41.302	.060
191—X	Jan. 24, 1929	278.960	240.213	250.331	1,200	720	24,135.6	85.0	3.8	24,224.4	23,934	41.234	−.008
193—X	Jan. 26, 1929	419.181	239.904	249.947	1,080	720	29,760.1	76.5	−.4	29,836.2	29,711	41.222	−.020
195—X	Jan. 31, 1929	421.532	239.937	250.017	1,080	720	29,974.3	76.5	1.0	30,051.8	29,814	41.236	−.006

Even-temperature interval 230°–240°. $Z]_{230}^{240}$=12,124.2 Int. joules. Mean value of $\alpha]_{230}^{240}=\alpha_m$=41.3025 Int. joules per g.

173—Y	Dec. 17, 1928	292.871	240.112	250.217	1,200	720	24,688.6	85.0	−.7	24,772.9	24,511	41.245	.003
174—Y	Dec. 18, 1928	408.332	240.262	250.209	1,140	720	29,030.4	80.7	−3.3	29,107.8	29,257	41.205	−.037
175—Y	Dec. 19, 1928	414.265	240.242	250.142	1,140	720	29,147.9	80.7	−3.6	29,225.0	29,515	41.238	−.004
176—Y	Dec. 20, 1928	279.315	239.850	249.857	1,140	720	23,886.7	80.8	−.6	23,966.9	23,955	41.256	.014
177—Y	Dec. 21, 1928	413.267	240.364	250.363	1,080	720	29,405.1	76.5	−1.5	29,480.1	29,472	41.234	−.008
178—Y	Dec. 26, 1928	288.124	240.229	250.289	1,200	720	24,379.1	85.0	−1.6	24,462.5	24,308	41.220	−.022
179—Y	Dec. 27, 1928	415.134	240.361	250.359	1,380	720	29,446.7	97.7	−2.2	29,542.2	29,537	41.205	−.037
181—Y	Dec. 29, 1928	419.612	240.268	250.295	1,080	720	29,769.5	76.5	−1.4	29,844.6	29,757	41.289	.047
183—Y	Jan. 2, 1929	285.531	240.422	250.441	1,200	720	24,166.5	85.0	−.1	24,251.4	24,192	41.188	−.054
184—Y	Jan. 3, 1929	286.319	240.245	250.234	1,140	720	24,143.0	80.7	−1.0	24,222.7	24,242	41.249	.007
189—Y	Jan. 22, 1929	420.292	240.120	249.914	1,020	720	29,116.2	52.7	.7	29,169.6	29,783	41.284	.042
190—Y	Jan. 23, 1929	277.212	240.215	250.225	1,140	720	23,852.5	58.9	.4	23,911.8	23,881	41.302	.060
191—Y	Jan. 24, 1929	278.960	240.213	250.331	1,200	720	24,135.6	85.0	3.8	24,224.4	23,934	41.234	−.008
193—Y	Jan. 26, 1929	419.181	239.904	249.947	1,080	720	29,760.1	76.5	−.4	29,836.2	29,711	41.222	−.020
195—Y	Jan. 31, 1929	421.532	239.937	250.017	1,080	720	29,974.3	76.5	1.0	30,051.8	29,814	41.236	−.006

Even-temperature interval 240°–250°. $Z]_{240}^{250}$=12,431.5 Int. joules. Mean value of $\alpha]_{240}^{250}=\alpha_m$=41.2423 Int. joules per g.

TABLE 3.—*Principal data from α experiments* $Q]_1^2 = M\alpha]_1^2 + Z]_1^2$. $\alpha]_1^2 = \left[H - L\frac{u}{u'-u}\right]_1^2$—Continued

Experiment No.	Date	Mass of water M	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Time of electric heating	Total electric energy	Pump energy	Heat leak	Entire energy added Q	Energy for even temperature intervals $Q]_1^2$	$\alpha]_1^2$	Residual $\alpha]_1^2 - \alpha_m$
		g	°C.	°C.	*Seconds*	*Seconds*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*
173–Z	Dec. 17, 1928	292.871	250.217	260.287	1,200	720	24,926.0	83.6	−2.7	25,006.9	24,825	41.162	0.035
174–Z	Dec. 18, 1928	408.332	250.209	260.169	1,260	720	29,356.5	87.8	−.9	29,443.4	29,555	41.107	−.029
175–Z	Dec. 19, 1928	414.265	250.142	260.129	1,200	720	29,690.6	83.6	−3.1	29,771.1	29,805	41.122	−.005
176–Z	Dec. 20, 1928	279.315	249.857	260.426	1,140	720	25,563.4	79.4	−1.8	25,641.0	24,255	41.120	−.007
177–Z	Dec. 21, 1928	413.267	250.363	260.285	1,260	720	29,464.0	87.9	−1.6	29,550.2	29,773	41.144	.017
178–Z	Dec. 26, 1928	288.124	250.289	260.266	1,260	720	24,469.0	87.8	−1.6	24,555.2	24,603	41.070	−.057
179–Z	Dec. 27, 1928	415.134	250.359	260.241	1,200	720	29,405.6	83.6	−2.5	29,486.7	29,830	41.096	−.031
181–Z	Dec. 29, 1928	419.612	250.295	260.163	1,260	720	29,555.1	87.8	.0	29,642.9	30,032	41.139	.012
183–Z	Jan. 2, 1929	285.531	250.441	260.077	1,260	720	23,545.0	87.8	.7	23,633.5	24,517	41.142	.015
184–Z	Jan. 3, 1929	286.319	250.234	260.181	1,080	720	24,345.3	75.2	−.3	24,420.2	24,544	41.123	−.004
189–Z	Jan. 22, 1929	420.292	249.914	259.932	1,080	720	30,067.2	54.9	.0	30,122.1	30,071	41.165	.038
190–Z	Jan. 23, 1929	277.212	250.225	260.210	1,320	720	24,094.0	67.2	1.0	24,162.2	24,192	41.204	.077
191–Z	Jan. 24, 1929	278.960	250.331	260.486	1,560	720	24,504.0	108.8	.9	24,613.7	24,226	41.068	−.059
195–Z	Jan. 31, 1929	421.532	250.017	260.048	1,140	720	30,115.8	79.4	.3	30,195.5	30,102	41.117	−.010
Even-temperature interval 250°–260°. $Z]_{250}^{260} = 12{,}769.7$ Int. joules. Mean value of $\alpha]_{250}^{260} = \alpha_m = 41.1273$ Int. joules per g.													
173–&	Dec. 17, 1928	292.871	260.287	270.374	1,460	720	25,288.1	100.0	−5.2	25,382.9	25,152	41.096	.034
174–&	Dec. 18, 1928	408.332	260.169	270.165	1,340	720	29,790.8	91.8	−6.9	29,875.7	29,882	41.059	−.003
175–&	Dec. 19, 1928	414.265	260.129	270.232	1,320	720	30,357.5	90.4	1.1	30,449.0	30,133	41.077	.015
176–&	Dec. 20, 1928	279.315	260.426	270.044	1,560	720	23,552.5	106.9	−1.4	23,658.0	24,590	41.078	.016
177–&	Dec. 21, 1928	413.267	260.285	270.200	1,320	720	29,748.4	90.4	.6	29,839.4	30,087	41.065	.003
178–&	Dec. 26, 1928	288.124	260.266	270.249	1,820	720	24,773.7	124.7	3.9	24,902.3	24,937	41.026	−.036
179–&	Dec. 27, 1928	415.134	260.241	270.114	1,380	720	29,673.9	94.5	−2.3	29,766.1	30,143	41.015	−.047
183–&	Jan. 2, 1929	285.531	260.077	269.831	1,500	720	24,121.0	102.7	2.0	24,225.7	24,839	41.056	−.006
184–&	Jan. 3, 1929	286.319	260.181	270.165	1,140	720	24,770.1	78.1	.8	24,849.0	24,883	41.096	.034
189–&	Jan. 22, 1929	420.292	259.932	270.044	1,440	720	30,650.3	71.8	.1	30,722.2	30,382	41.080	.018
190–&	Jan. 23, 1929	277.212	260.210	270.122	1,380	720	24,217.7	68.8	3.5	24,290.0	24,500	41.065	.003
191–&	Jan. 24, 1929	278.960	260.486	270.255	1,080	720	23,927.6	73.9	.5	24,002.0	24,557	41.012	−.050
195–&	Jan. 31, 1929	421.532	260.048	269.958	1,080	720	30,080.7	74.0	1.4	30,156.1	30,429	41.071	.009
Even-temperature interval 260°–270°. $Z]_{260}^{270} = 13{,}116.3$ Int. joules. Mean value of $\alpha]_{260}^{270} = \alpha_m = 41.0618$ Int. joules per g.													

TABLE 3 (appendix).—*Principal data from α experiments conducted over intervals of more than 10°*

Energy for

TABLE 3 (appendix).—*Principal data from α experiments conducted over intervals of more than 10°*

Experiment No.	Date	Mass of water, M	Initial temperature, θ_1	Final temperature, θ_2	Total time of experiment	Time of electric heating	Total electric energy	Pump energy	Heat leak	Entire energy added, Q	Even-temperature interval	Energy for even-temperature interval, Q_1^2
		g	°C	°C	Seconds	Seconds	Int. joules	Int. joules	Int. joules	Int. joules	°C	Int. joules
45	July 14, 1927	326.833	9.209	40.071	2,760	1,860	67,878.1	205.7	2.6	68,086.4	10- 40	66,189.6
45	----do----	326.833	40.071	70.327	2,880	1,800	67,030.5	186.0	6.9	67,223.4	40- 70	66,649.2
45	----do----	326.833	70.327	99.590	2,760	1,740	65,455.7	212.0	5.3	65,673.0	70-100	67,323.7
46	July 16, 1927	326.833	39.576	69.960	3,060	1,740	67,285.2	196.0	6.9	67,488.1	40- 70	66,638.6
46	----do----	326.833	69.960	99.945	2,580	1,740	67,094.2	154.0	5.9	67,254.1	70-100	67,284.3
51	July 25, 1927	493.054	70.093	100.031	2,940	1,800	87,736.7	178.0	4.9	87,919.6	70-100	88,094.9
53	July 27, 1927	493.054	1.628	19.809	3,720	1,080	52,505.8	222.4	3.5	52,731.7	0- 20	58,020.6
54	July 28, 1927	493.054	.826	99.790	8,040	6,180	288,001.5	593.6	12.1	288,607.2	0-100	291,612.9
55	July 29, 1927	493.054	.604	99.477	8,160	6,120	287,696.3	595.3	10.8	288,302.4	0-100	291,588.2
56	Aug. 1, 1927	291.001	6.304	58.267	3,120	2,100	106,856.5	222.8	7.3	107,086.6	0- 60	123,643.4
56	----do----	291.001	58.267	79.908	6,120	1,380	44,869.7	190.7	5.9	45,066.3	60- 80	41,657.6
60	Aug. 5, 1927	291.001	.586	100.048	6,780	5,940	205,734.5	464.9	4.0	206,203.4	0-100	207,253.0
67	Sept. 26, 1927	495.653	1.041	99.483	7,380	6,300	287,605.5	505.2	9.0	288,119.7	0-100	292,688.8
68	Sept. 29, 1927	507.031	.949	99.607	6,900	5,760	292,942.9	479.5	10.3	293,432.7	0-100	297,430.0
69	Sept. 30, 1927	507.031	.682	99.950	6,960	5,880	294,750.4	474.7	14.2	295,239.3	0-100	297,413.0
70	Oct. 3, 1927	275.167	.560	99.755	7,680	6,420	198,535.0	524.4	15.3	199,074.7	0-100	200,689.6
71	Oct. 4, 1927	275.167	.766	100.153	7,560	5,820	198,896.7	506.2	13.7	199,416.6	0-100	200,629.6
72	Oct. 5, 1927	275.167	.445	99.716	7,560	[1] 5,820	198,594.6	540.8	18.7	199,154.1	0-100	200,620.5
73	Oct. 6, 1927	498.832	.817	99.728	7,800	[1] 6,120	290,209.4	549.2	17.0	290,775.6	0-100	293,974.5
74	Oct. 7, 1927	498.832	.826	100.325	8,460	[1] 6,120	291,980.6	512.6	15.9	292,509.1	0-100	293,965.5
75	Oct. 8, 1927	498.832	.795	100.311	8,700	[1] 6,180	291,935.5	594.0	20.0	292,549.5	0-100	293,958.1
77	Oct. 13, 1927	258.324	.549	100.160	8,700	[1] 5,940	192,202.0	639.8	18.7	192,860.5	0-100	193,595.3
78	Oct. 14, 1927	258.324	.595	100.319	9,480	[1] 6,000	192,542.5	523.2	17.4	193,083.1	0-100	193,594.7
80	Oct. 24, 1927	268.054	.834	99.893	8,040	[1] 6,120	195,210.7	581.5	19.7	195,811.9	0-100	197,658.5
81	Oct. 25, 1927	268.054	.789	99.787 [7]	7,740	[1] 6,000	195,104.4	559.9	15.7	195,680.0	0-100	197,652.1
82	Oct. 26, 1927	268.054	.670	100.042	7,980	[1] 6,060	195,854.1	577.2	15.0	196,446.3	0-100	197,672.1
83	Oct. 27, 1927	268.054	.506	99.943	8,100	[1] 6,000	195,974.6	582.0	13.6	196,570.2	0-100	197,675.6
84	Oct. 28, 1927	475.116	.786	100.353	8,100	6,060	282,255.8	592.8	13.5	282,862.1	0-100	284,074.3
85	Oct. 29, 1927	475.116	.927	100.068	8,220	6,000	281,037.0	593.9	12.4	281,643.3	0-100	284,073.6
86	Nov. 7, 1927	475.903	100.523	198.456	8,340	7,320	287,655.2	457.1	25.9	288,138.2	100-200	294,320.1
91	Nov. 12, 1927	475.903	100.091	200.368	13,140	8,220	294,532.8	533.7	−7.9	295,058.6	100-200	294,403.2
115	Feb. 6, 1928	419.333	149.990	199.855	6,480	5,880	136,532.9	343.0	−0.8	136,875.1	150-200	137,246.6
116	Feb. 11, 1928	388.753	99.958	199.817	1,086	10,200	257,020.1	605.0	2.2	257,627.3	100-200	258,010.8
185	Jan. 4, 1929	418.892	200.124	270.546	5,820	5,100	207,129.6	419.0	−6.4	207,542.2	200-270	206,249.0

See footnote 1, p. 445.

The entire energy added, Q, is the sum of the total electric energy, pump energy, and heat leak. This entire energy actually added is adjusted to the value it would have had for the even-temperature interval, which was approximated, giving the values of $Q]_1^2$. The calculation of α_m, the mean value of α for an entire group of experiments follows next. This is a least-square calculation, using the formula

$$Q]_1^2 = M\alpha]_1^2 + Z]_1^2$$

This reduction, using the entire group of values of M and $Q]_1^2$ for a single temperature interval, yields the mean value α_m and $Z]_1^2$. Using this value of $Z]_1^2$, which is a constant for the calorimeter as used, the individual values of $\alpha]_1^2$ for each experiment are next computed and compared with the mean for the group.

In the last section of Table 3 the principal data are assembled from those α experiments which were carried out in intervals of more than 10° C. A considerable number of these, particularly between 0 and 100° were made in 100° nonstop experiments which serve as control experiments, adding greater certainty to the values at 100 and 200° C. than the experiments in shorter installments alone give.

In order best to utilize the whole aggregate of α experiments, the results are assembled in Table 4 for the purpose of computing the values of the change in α from 0 to 100, from 100 to 200, and from 200 to 270 from the entire series of energy measurements. With very few exceptions the energy account for each of these three large intervals was kept continuously, the stops at the intermediate 100 points for observing temperatures being made for the purpose of independently establishing these intermediate values of α, but without interruption of the heat-leak and pump-energy control.

TABLE 4.—CALCULATION OF MEAN VALUE OF [illegible]

Experiment No.	Mass of water M	Energy added for even-temperature interval, Q_1^2, Int. joules										$\Sigma Q_1^2 = Q_0^{100}$	α_0^{100}	Residual $\alpha_0^{100} - \alpha_m$
		0°–10°	10°–20°	20°–30°	30°–40°	40°–50°	50°–60°	60°–70°	70°–80°	80°–90°	90°–100°			
	g													
42	326.833	22,032.0	22,025.8									222,124.8	417.125	−0.232
43	326.833			22,061.9	22,100.6	22,153.5	22,210.1	22,278.1	22,342.4	22,420.2	22,500.2	222,201.5	417.360	.003
44	326.833			←66,189.6→		←66,649.2→			←67,323.7→			222,142.9	417.181	−.176
45	326.833	22,039.0				←66,638.6→			←67,284.3→					
46	326.833	22,033.8	22,024.7	22,057.9	22,103.6									
49	493.054	29,033.6	28,979.0	29,005.8	29,047.4	29,084.1	29,158.3	29,214.1	29,285.6					
50	493.054							29,212.5	29,280.5	29,350.0	29,450.9	291,603.7	417.417	.060
51	493.054	29,026.6	28,980.9	28,998.2	29,043.4	29,093.6	29,147.2	29,212.3	←88,094.9→			291,597.1	417.404	.047
53	493.054	←58,020.6→		29,002.7	29,044.9	29,089.2	29,148.7	29,209.0	29,282.3	29,357.5	29,444.5	291,599.4	417.408	.051
54	493.054											291,612.9	417.436	.079
55	493.054	←123,643.4→						←41,657.6→		20,936.7	21,030.2	291,588.2	417.386	.029
56	291.001	20,555.7	20,538.7	20,572.5	20,616.8	20,667.0	20,740.0	20,787.0	20,861.5	20,941.0	21,029.1	207,267.9	417.433	.076
57	291.001	20,543.6	20,542.2	20,576.8	20,619.7	20,660.6	20,727.9	20,791.6	20,858.0	20,934.6	21,023.0	207,309.3	417.575	.218
58	291.001	20,546.7	20,539.5	20,583.8	20,632.5	20,673.2	20,734.2	20,798.2	20,869.7	20,948.7	21,028.8	207,278.0	417.468	.111
59	291.001											207,355.3	417.733	.376
60	366.801	23,710.6	23,699.9	23,732.4	23,774.0	23,821.9	23,884.6	23,947.5	24,016.4	24,093.9	24,180.6	207,253.0	417.382	.025
62	366.801	23,702.8	23,699.3	23,731.4	23,765.2	23,818.3	23,880.7	23,947.4	24,015.3	24,088.1	24,178.3	238,861.8	417.303	−.054
63	495.653											238,826.8	417.208	−.149
67	507.031											292,688.8	417.418	.061
68	507.031											297,430.0	417.402	.045
69	275.167											297,413.0	417.368	.011
70	275.167											200,689.6	417.546	.189
71	275.167											200,629.6	417.329	−.028
72	275.167											200,620.5	417.296	−.061
73	498.832											293,974.5	417.335	.022
74	498.832											293,965.5	417.317	−.040
75	498.832											293,958.1	417.302	−.055
77	258.324											193,595.3	417.308	−.049
78	258.324											193,594.7	417.306	−.051
80	268.054											197,658.5	417.319	−.038
81	268.054											197,652.1	417.295	−.062
82	268.054											197,672.1	417.370	.013
83	268.054											197,675.6	417.383	.026
84	475.116											284,074.3	417.329	−.028
85	475.116											284,073.6	417.328	−.029

Even-temperature interval 0°–100°. $Z_0^{100} = 85{,}794.5$ Int. joules. Mean value of $\alpha_0^{100} = \alpha_m = 417.357$ Int. joules per g.

NOTE.—The results of experiments 42 to 60, inclusive, were obtained in the earlier stages of the work and were given one-quarter the weight of the later results.

CALCULATION OF MEAN VALUE OF $\left[H-L-\frac{u}{u'-u}\right]_{100}^{200}$—Continued

Experiment No.	Mass of water M	Energy added for even temperature interval, Q_1^2 Int. joules										$\Sigma Q_1^2 = Q_0^{100}$	α_{100}^{200}	Residual $\alpha_{100}^{200}-\alpha_m$
		100°–110°	110°–120°	120°–130°	130°–140°	140°–150°	150°–160°	160°–170°	170°–180°	180°–190°	190°–200°			
	g													
86	475.903											294,320.1	416.817	−0.056
87	475.903	28,823.8	28,927.0	29,046.4	29,177.4	29,305.7								
88	475.903						29,459.1	29,624.3	29,798.0	29,988.4	30,197.2	294,347.3	416.874	.001
89	475.903	28,825.7	28,929.7	29,046.2	29,175.5	29,312.8	29,466.3	29,623.7	29,813.2	29,997.7	30,196.1	294,386.9	416.957	.084
90	475.903	28,825.4	28,928.8	29,047.9	29,170.2	29,314.5	29,461.4	29,627.2	29,805.0	29,983.1	30,208.7	294,372.2	416.927	.054
91	475.903											294,403.2	416.992	.119
95	267.764	20,144.5	20,251.9	20,365.8	20,493.7	20,633.6	20,763.0	20,950.2	21,129.4	21,326.3	21,535.9	207,594.3	416.929	.056
96	267.764	20,144.5	20,249.9	20,364.9	20,492.7	20,625.5	20,785.8	20,945.6	21,128.8	21,319.6	21,523.3	207,580.6	416.878	.005
97	267.764	20,150.2	20,247.5	20,369.0	20,493.8	20,631.5	20,795.4	20,933.6	21,122.2	21,315.9	21,531.3	207,590.5	416.915	.042
112	301.182	21,542.1	21,650.2	21,760.8	21,887.6	22,031.1	22,180.1	22,341.1	22,519.1	22,706.9	22,909.8	221,528.8	416.985	.062
113	410.025	26,077.0	26,183.1	26,297.6	26,423.3	26,567.4	26,714.0	26,874.1	27,052.5	27,238.4	27,436.9	266,864.9	416.827	−.046
114	410.025	26,066.3	26,173.2	26,291.8	26,417.9	26,559.3	26,706.4	26,873.3	27,045.7	27,238.1	27,440.4	266,812.4	416.698	−.175
115	419.333	26,457.4	26,565.8	26,681.6	26,812.7	26,951.9	←		137,246.6		→	270,716.0	416.758	−.115
116	388.753											258,010.8	416.859	−.014

Even-temperature interval 100°–200°. Z_{100}^{200}=95,955.6 Int. joules. Mean value of $\alpha_{100}^{200}=\alpha_m$=416.873 Int. joules per g.

CALCULATION OF MEAN VALUE OF $\left[a\right]_{200}^{270}$ = a_m = [illegible]

Experiment No.	Mass of water, M	Energy added for even temperature interval, $Q]_1^2$ Int. joules							$\Sigma Q]_1^{II}$ / $Q]_{200}^{270}$	$a]_{200}^{270}$	Residual $a]_{200}^{270} - a_m$
		200°–210°	210°–220°	220°–230°	230°–240°	240°–250°	250°–260°	260°–270°			
173	292.871	23,464	23,701	23,957	24,233	24,511	24,825	25,152	169,843	289.276	0.199
174	408.332	28,243	28,473	28,715	28,986	29,257	29,555	29,882	203,111	288.952	−.122
175	414.265	28,486	28,718	28,954	29,226	29,515	29,805	30,133	204,837	288.980	−.097
176	279.315	22,900	[1] (23,131)	23,390	23,665	23,955	24,255	24,590	165,886	289.148	.071
177	413.267	28,472	28,675	28,941	29,193	29,472	29,773	30,087	204,613	289.136	.059
178	288.124	23,264	23,504	23,759	24,019	24,308	24,603	24,937	168,394	289.013	−.064
179	415.134	28,537	28,755	29,004	29,264	29,537	29,830	30,143	205,070	288.937	−.140
183	285.531	23,144	23,384	23,632	23,900	24,192	24,517	24,839	167,608	288.885	−.192
184	286.319	23,192	23,428	23,686	23,958	24,242	24,544	24,883	167,933	289.225	.148
185	418.892								206,249	289.159	.089
189	420.292	28,757	28,989	29,230	29,494	29,783	30,071	30,382	206,706	289.283	.206
190	277.212	22,832	23,054	23,312	23,577	23,881	24,192	24,500	165,348	289.401	.324
191	278.960	22,888	23,115	23,376	23,640	23,934	24,226	24,557	165,636	288.620	−.457
192	419.602		28,935								
195	421.532	28,796	29,024	29,272	29,534	29,814	30,102	30,429	206,971	289.061	−.016

Even temperature interval 200°–270°. $Z]_{200}^{270}$=85,122.5 Int. joules. Mean value of $a]_{200}^{270}$=a_m=289.077 Int. joules per g.

[1] Calculated from experiment 192.

The independent determinations of $\alpha]_0^{100}$, $\alpha]_{100}^{200}$, and $\alpha]_{200}^{270}$ are co
puted in Table 4 after summing up the total energy added in e
entire experiment. The calculations for α_m and Z are made
these groups of data by least-square reduction, in the same ma
as for the 10° groups in Table 3. The value for each individual
periment is then calculated and the deviations from the mean fou

The next step in Table 5 in the reduction is the adjustment of
10° values of α, taking into account the results of the last calcula
of the change in α between the temperatures of 0°, 100°, 200°,
270° C. This adjustment consists in distributing the discrepa
between the 10° steps and the 100° or 70° steps proportionately,
as to make the adjusted values of the 10° steps add up to the s
value as the overall. Having so adjusted the intermediate val
they are next summed up, giving as the result of this entire group o
experiments the table of values of $H-L\frac{u}{u'-u}$ at each multiple of
reckoned from 0° C.

TABLE 5.—*Adjustment of values of* $\left[H-L\frac{u}{u'-u}\right]$ *and assembly of final va*
reckoned from 0° C.

| Temperature interval (°C.) | Mean value of $\alpha]_1^2$ | Adjusted value of $\alpha]_1^2$ | Final adjusted value of $\alpha]_0^\theta$ | Tem
atu |
|---|---|---|---|---|
| | *Joules/g* | *Joules/g* | *Joules/g* | °C |
| 0–10 | 41.984 | 41.989 | 41.989 | |
| 10–20 | 41.802 | 41.808 | 83.797 | |
| 20–30 | 41.708 | 41.714 | 125.511 | |
| 30–40 | 41.704 | 41.709 | 167.220 | |
| 40–50 | 41.698 | 41.704 | 208.924 | |
| 50–60 | 41.683 | 41.688 | 250.612 | |
| 60–70 | 41.683 | 41.689 | 292.301 | |
| 70–80 | 41.685 | 41.690 | 333.991 | |
| 80–90 | 41.666 | 41.671 | 375.662 | |
| 90–100 | 41.690 | 41.695 | | |
| Total | 417.303 | 417.357 | 417.357 | |
| 0–100 | 417.357 | | | |
| 100–110 | 41.678 | 41.678 | 459.04 | |
| 110–120 | 41.684 | 41.683 | 500.72 | |
| 120–130 | 41.677 | 41.676 | 542.39 | |
| 130–140 | 41.700 | 41.700 | 584.09 | |
| 140–150 | 41.713 | 41.712 | 625.81 | |
| 150–160 | 41.703 | 41.702 | 667.51 | |
| 160–170 | 41.712 | 41.712 | 709.22 | |
| 170–180 | 41.701 | 41.701 | 750.92 | |
| 180–190 | 41.658 | 41.658 | 792.58 | |
| 190–200 | 41.651 | 41.651 | | |
| Total | 416.877 | 416.873 | 834.23 | |
| 100–200 | 416.873 | | | |
| 200–210 | 41.503 | 41.519 | 875.75 | |
| 210–220 | 41.391 | 41.407 | 917.16 | |
| 220–230 | 41.338 | 41.354 | 958.51 | |
| 230–240 | 41.302 | 41.318 | 999.83 | |
| 240–250 | 41.242 | 41.258 | 1,041.09 | |
| 250–260 | 41.127 | 41.143 | 1,082.23 | |
| 260–270 | 41.062 | 41.078 | | |
| Total | 288.966 | 289.077 | 1,123.31 | |
| 200–270 | 289.077 | | | |

...o adjustment for smoothing the trend of values has, up to this ...t, been introduced into the reduction. This will be undertaken ...er the head of formulation, to be described later.

2. GAMMA EXPERIMENTS

...n example of the record of a single determination of γ, equal to $\frac{u'}{u'-u}$, is given in Table 6. The total time of the experiment in ... case is the time between the automatic shifting of the flow of ...or from the spill to the receiver, and the shifting to the next ...iver, and applies to the electric heating, the pump energy, and ... heat leak. The temperature readings are so distributed as to ... the initial and final temperatures at these instants of starting ... stopping the experiment. The readings of the thermometer with ...s in the n position and of the thermoelements 1 to 5 were taken at ...inute intervals during the experiment. These readings serve to ...ermine the vraiation of temperature of the calorimeter during the ...eriment.

TABLE 6.—*Data sheet—determination of* $L\frac{u'}{u'-u}$

Experiment No. 273-A. November 16, 1929, at 270° C.
Observers: N. S. O., E. F. F., D. C. G.

Time	Thermometers. Bridge readings		Thermoelements		Electric power	
	2n	2r	t. e. 1-5	Regulating[1]	*I*	*E*
	Ohms	*Ohms*	*μv*	*μv*	*Amperes*	*Volts*
...00						
...30	51.8960		9.7			
...40	51.8959		7.8			
...50	51.8959		6.0			
...00				(−3)		Start.
...10		51.9027	4.0			
...20		51.9028	3.6			
...30		51.9027	3.8			
...00	51.8960		5	−2		21.999
...00	51.8958		8	(−1)	2.1549	
...00	51.8964		10	1		21.997
...00	51.8966		10	−1	2.1547	
...00	51.8965		7	(−2)		21.996
...00	51.8964		9	0	2.1547	
...00	51.8964		12	(1)		21.996
...00	51.8965		9	(−1)	2.1547	
...00	51.8964		13	(2)		21.995
...00	51.8971		13	(2)	2.1546	
...00	51.8970		9	(−1)		21.995
...00	51.8958		11	(1)	2.1545	
...00	51.8957		13	(2)		21.993
...00	51.8958		6	−4	2.1544	
...00	51.8956		6	(−2)		21.992
...00	51.8956		8	(−1)	2.1543	
...00	51.8958		7	(−2)		21.991
...00	51.8957		8	(−1)	2.1542	
...00	51.8956		10	(0)		21.990
...00	51.8956		10	1	2.1541	
...00	51.8951		11	(1)		21.989
...00	51.8951		7	(−2)	2.1541	
...30	51.8954		6.8			
...40	51.8957		6.4			
...50	51.8958		6.9			
...00				(−2)		Stop.
...10		51.9028	8.7			
...20		51.9028	9.2			
...30		51.9030	9.8			

...alues in parentheses calculated from indications of t. e. 1-5.
...otal heat-leak factor = −14 mv-min. Total time of experiment and electric heating = 1,380 seconds

A reduction, showing the calculation of γ, is given in Table 7. T reduction makes use of the formula:

$$\gamma_1=\frac{1}{\Delta M}(Q_E+Q_P+Q_L-[Z+M_2\alpha]^2_1)+\frac{\Delta H'}{\Delta\theta}(\theta_1-\theta_m)$$

in which Q_E, Q_P, and Q_L denote the amounts of energy added elec cally, by the pump, and by heat leak, respectively. The te $[Z+M_2\alpha]^2_1$ expresses the energy correction for the difference of final temperature of the calorimeter and its contents from the init The last term expresses the energy correction for variation in temperature of steam withdrawn. This correction was found to in every case less than 0.00001 of the whole, and has been omit from the final calculation of γ.

TABLE 7.—*Computation–determination of* $L\frac{u'}{u'-u}$

EXPERMINENT No. 273-A

Temperature	Initial	Fi
$(n+r)/2$ on bridge	51.89933	51.
Bridge correction	.01168	.
R_θ	51.91101	51.
$R_\theta-R_o$	26.30321	26.
$100\ (R_\theta-R_o)/(R_{100}-R_o)$	263.2320	263.
$0.01\theta(0.01\theta-1)\delta$	6.7999	6.
Reference block temperature	270.0319	270.
Mean t. e. 1–5 (microvolts)	5.82	7.
Mean t. e. 1–5 (degrees)	−.0189	−
Temperature of calorimeter	270.0130	270.

CALCULATION OF ENERGY

Potentiometer	Current		Volt
Mean reading	2.15447	Mean reading	21.
Potentiometer correction	.00020	Potentiometer correction	.
Correction for standard 0.01 ohm	−.00011	Correction for volt-box factor	.
Correction for volt-box current	−.00066		
Current=I	2.15390	Voltage=E	22.

Time of experiment=t=1,380 seconds.	
Total electric energy=$IE2$	65,401.9 joul
Pump power=0.0477 watts.	
Pump energy	65.8 joul
Total heat-leak factor=−14 microvolt-minutes.	
Heat-leak coefficient=0.156 joule/microvolt-minute.	
Heat leak	−2.2 joul
Change in calorimeter temperature=−0.0068°	
Factor for calorimeter temperature change=2,636 joules/degree.	
Energy for calorimeter temperature change	17.9 joul
Total energy for evaporation	65,483.4 joul
Mass withdrawn=39.364 g.	
$L\frac{u'}{u'-u}$ at 270.0130°	1,663.54 joul

The principal data from the gamma experiments are assembled Table 8 and the computation of γ completed for the entire series.

$$\gamma_1 = \frac{1}{\Delta M}\{Q_E + Q_P + Q_L - [Z + M_2\alpha]_1^2\} + \frac{\Delta U}{\Delta\theta}(\theta_1 - \theta_m)$$

Experiment No.	Date	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Mass of vapor removed ΔM	Mass of water remaining M_2	Total electric energy Q_E	Pump energy Q_P	Heat leak Q_L	Energy correction for final temperature difference $-[Z+M_2\alpha]_1^2$	Entire energy added	Entire energy per gram γ_1	γ_θ corrected to even temperature	Residual $\gamma_\theta - \gamma_m$
		° C.	° C.	*Minutes*	*g*	*g*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*
228-A	May 25, 1929	99.956	99.941	60	28.631	360.9	64,434.8	226.2	−6.5	36.2	64,690.7	2,259.46	2,259.35	0.64
228-B	do	99.941	99.946	60	28.591	332.3	64,380.9	226.2	−8.9	−12.4	64,585.8	2,258.95	2,258.80	.09
228-C	do	99.946	99.941	60	28.576	303.7	64,345.3	226.2	−1.8	11.1	64,580.8	2,259.96	2,259.82	1.11
229-A	May 28, 1929	99.959	99.957	30	28.905	348.3	65,170.9	113.1	−1.2	40.9	65,323.7	2,259.94	2,259.83	1.12
229-B	do	99.957	99.962	30	28.903	319.4	65,189.4	113.1	−1.6	−11.7	65,289.3	2,258.91	2,258.80	.09
229-C	do	99.962	99.984	30	28.896	290.5	65,192.5	113.1	−5.9	−48.3	65,251.4	2,258.15	2,258.05	−.66
229-D	do	99.984	99.969	16	15.433	275.0	34,770.2	60.3	−1.1	32.4	34,861.8	2,258.91	2,258.87	.16
231-A	June 8, 1929	99.862	99.844	30	29.400	320.7	66,257.3	113.1	−2.0	42.4	66,410.8	2,258.87	2,258.50	−.21
231-B	do	99.844	99.833	30	29.395	291.3	66,230.4	113.1	3.4	23.0	66,369.9	2,257.86	2,257.45	−1.26
232-A	June 11, 1929	99.966	99.949	20	30.651	374.7	69,101.1	75.4	−5.5	42.3	69,213.3	2,258.11	2,258.02	−.69
232-B	do	99.949	99.949	21	32.165	342.5	72,558.9	79.2	1.3	−.2	72,639.2	2,258.33	2,258.19	−.52
232-C	do	99.949	99.938	20	30.634	311.9	69,095.4	75.4	1.9	25.9	69,198.6	2,258.88	2,258.74	.03
232-D	do	99.938	99.957	20	30.604	281.3	69,087.9	75.4	−1.1	−40.9	69,121.3	2,258.57	2,258.41	−.30
233-A	June 12, 1929	100.010	100.020	22	22.562	407.4	50,903.5	82.9	−.4	−25.5	50,960.5	2,258.69	2,258.72	.01
233-B	do	100.001	99.987	21	32.178	373.9	72,566.8	79.2	−2.5	36.7	72,680.2	2,258.69	2,258.69	−.02
233-C	do	99.987	99.982	20	50.646	343.3	69,112.4	75.4	−1.8	11.5	69,197.5	2,257.96	2,257.93	−.78
233-D	do	99.982	99.995	20	30.611	312.7	69,113.2	75.4	0	−30.3	69,158.3	2,259.26	2,259.21	.51
233-E	do	99.995	100.001	20	30.615	282.1	69,114.9	75.4	−3.3	−13.2	69,173.8	2,259.47	2,259.46	.75
234-A	June 13, 1929	99.986	100.000	40	39.074	311.3	88,105.2	150.8	−.4	−30.4	88,225.2	2,257.90	2,257.86	−.85

Even temperature 100°. Z_{100}=956.3 Int. joules/° C. α_{100}=4.169 Int. joules per g° C. Mean value of $\gamma_{100}=\gamma_m$=2,258.71 Int. joules per g.

TABLE 8.—*Principal data from γ experiments*—Continued

$$\gamma_1=\frac{1}{\Delta M}\{Q_H+Q_P+Q_L-[Z+M_2\alpha]_1^2\}+\frac{\Delta H'}{\Delta\theta}(\theta_1-\theta_m)$$

Experiment No.	Date	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Mass of vapor removed ΔM	Mass of water remaining M_2	Total electric energy Q_H	Pump energy Q_P	Heat leak Q_L	Energy correction for final temperature difference $-[Z+M_2\alpha]_1^2$	Entire energy added	Entire energy per gram γ_1	γ_θ corrected to even temperature	Residual $\gamma_\theta-\gamma_m$
		° C.	° C.	Minutes	g	g	Int. joules	Int. joules	Int. joules	Int. joules	Int. joules	Int. joules/g	Int. joules/g	Int. joules/g
213–A	Apr. 22, 1929	129.939	129.949	30	29.708	367.8	64,536.6	153.6	−6.0	−24.7	64,659.5	2,176.50	2,176.33	−0.82
213–B	do	129.949	129.950	30	29.723	338.1	64,535.9	153.6	−4.0	−1.9	64,683.6	2,176.21	2,176.07	−1.07
225–A	May 22, 1929	129.915	129.908	30	31.207	375.1	67,802.1	109.8	7.7	16.0	67,935.6	2,176.93	2,176.69	−.46
225–B	do	129.908	129.924	30	31.151	343.9	67,813.0	109.8	−6.9	−37.8	67,878.1	2,179.00	2,178.74	1.59
225–C	do	129.924	129.912	30	31.206	312.7	67,789.9	109.8	7.6	26.9	67,934.2	2,176.96	2,176.75	−.40
225–D	do	129.912	129.932	30	31.143	281.6	67,740.3	109.8	3.0	−41.6	67,811.5	2,177.42	2,177.13	−.02
226–A	May 23, 1929	129.943	129.934	30	30.982	344.9	67,326.1	109.8	−2.9	22.6	67,455.6	2,177.25	2,177.09	−.06
226–B	do	129.934	129.944	30	30.963	313.9	67,315.7	109.8	−1.8	−23.9	67,399.8	2,176.79	2,176.60	−.55
226–C	do	129.944	129.931	30	30.953	283.0	67,258.9	109.8	−.5	28.7	67,396.9	2,177.39	2,177.23	.08
226–D	do	129.931	129.949	15	15.447	267.5	33,627.7	54.9	.1	−37.3	33,645.4	2,178.12	2,177.93	.78
227–A	May 24, 1929	129.944	129.934	60	31.037	347.0	67,343.2	219.6	−9.3	22.9	67,576.4	2,177.29	2,177.13	−.02
227–B	do	129.937	129.906	15	28.583	300.6	62,108.1	54.9	−1.4	69.6	62,231.2	2,177.21	2,177.03	−.12
227–C	do	129.906	129.917	15	28.527	272.0	62,076.4	54.9	−1.3	−23.2	62,106.8	2,177.12	2,176.87	−.28
235–A	June 14, 1929	129.986	129.986	20	32.752	379.3	71,267.5	73.2	−1.2	1.0	71,340.5	2,178.20	2,178.16	1.01
235–B	do	129.986	129.967	20	32.773	346.5	71,251.1	73.2	−1.0	44.1	71,367.4	2,177.63	2,177.59	.44
235–C	do	129.967	129.979	20	32.739	313.8	71,227.1	73.2	−.3	−26.8	71,273.2	2,177.01	2,176.92	−.23
235–D	do	129.979	129.976	20	32.728	281.0	71,189.7	73.2	−.7	7.3	71,269.5	2,177.63	2,177.57	.42
235–E	do	129.976	129.972	20	32.707	248.3	71,154.6	73.2	−1.0	7.7	71,234.5	2,177.96	2,177.90	.75
236–A	June 17, 1929	129.994	130.000	31	30.877	350.6	67,132.3	113.5	4.1	−15.5	67,234.4	2,177.49	2,177.47	.32
236–B	do	130.000	129.989	31	30.904	319.7	67,139.0	113.5	1.1	28.9	67,282.5	2,177.15	2,177.15	.00
236–C	do	129.989	129.985	31	30.885	288.8	67,145.6	113.5	−2.3	9.0	67,265.8	2,177.94	2,177.91	.76
236–D	do	129.985	130.000	31	30.877	257.8	67,128.4	113.5	4.9	−37.4	67,209.4	2,176.68	2,176.64	−.51
264–A	Oct. 12, 1929	130.021	130.015	30	29.317	372.9	63,681.2	109.8	−4.5	17.0	63,803.5	2,176.33	2,176.39	−.76
264–B	do	130.015	129.997	30	29.284	343.6	63,593.6	109.8	−4.9	42.7	63,741.2	2,176.66	2,176.70	−.45
264–C	do	129.997	130.015	30	29.207	314.4	63,530.6	109.8	−5.5	−41.4	63,593.5	2,177.34	2,177.33	.18
264–D	do	130.015	129.996	30	29.246	285.2	63,487.4	109.8	−5.7	41.2	63,632.7	2,175.58	2,175.62	−1.53
264–E	do	129.996	130.024	30	29.167	256.0	63,452.9	109.8	−5.1	−50.8	63,506.8	2,177.15	2,177.14	.01
265–F	do	130.024	130.021	30	29.178	226.8	63,444.6	109.8	−4.9	7.2	63,556.7	2,177.53	2,177.52	.39
247–A	July 25, 1929	149.960	149.966	60	29.036	387.4	61,344.6	215.4	5.3	−15.3	61,550.0	2,119.78	2,119.66	.02
		150.027	150.010	20	39.983	304.9	84,592.9	71.8	−.1	40.3	84,704.9	2,118.52	2,118.60	−1.04
														.09

247–A	July 25, 1929	149.960	149.966	60	29.036	387.4	61,344.6	215.4	5.3	−15.3	64,550.0	2,119.78	2,119.66	.02
247–B	do	150.027	150.010	20	39.983	304.9	84,592.9	71.8	−.1	40.3	84,704.9	2,118.52	2,118.60	−1.04
247–C	do	150.010	149.999	21	42.193	262.8	89,334.7	75.4	3.5	22.7	89,436.3	2,119.70	2,119.73	.09
248–A	July 26, 1929	150.013	150.006	15	30.331	367.8	64,209.0	53.9	−.7	19.9	64,282.1	2,119.35	2,119.39	−.25
248–B	do	150.006	150.012	15	30.309	337.4	64,190.7	53.9	2.2	−14.8	64,232.0	2,119.24	2,119.26	−.38
248–C	do	150.006	150.010	15	30.304	276.7	64,173.6	53.9	−1.7	−10.4	64,215.4	2,119.04	2,119.06	−.58
248–D	do	150.010	150.010	15	30.296	246.4	64,160.2	53.9	3.0	1.2	64,218.3	2,119.70	2,119.73	.09
261–A	Sept. 26, 1929	149.943	149.976	30	31.091	367.1	65,909.7	97.8	−6.8	−83.7	65,917.0	2,120.13	2,119.96	.32
261–B	do	149.976	149.960	31	32.158	334.9	68,040.2	101.1	−9.4	37.9	68,169.8	2,119.84	2,119.77	.13
261–C	do	149.960	149.948	30	31.083	303.9	65,782.3	97.8	−3.6	28.4	65,904.9	2,120.29	2,120.17	.53
261–D	do	149.948	149.977	30	31.008	272.8	65,734.9	97.8	−8.5	−62.8	65,761.4	2,120.79	2,120.64	1.00
261–E	do	149.977	149.983	30	31.028	241.8	65,708.4	97.8	−7.0	−13.4	65,785.8	2,120.21	2,120.14	.50
261–F	do	149.983	149.985	30	31.027	210.8	65,697.4	97.8	−6.6	−3.4	65,785.2	2,120.26	2,120.21	.57
263–A	Oct. 11, 1929	149.959	149.978	30	29.457	327.6	62,356.5	107.7	−.4	−45.8	62,418.0	2,118.95	2,118.83	−.81
263–B	do	149.966	149.962	30	29.407	268.6	62,196.1	107.7	−1.1	9.4	62,312.1	2,118.95	2,118.85	−.79
263–C	do	149.962	149.961	30	29.371	239.2	62,111.2	107.7	−3.4	.6	62,216.1	2,118.28	2,118.17	−1.47
263–D	do	149.961	149.959	30	29.303	209.9	62,038.6	107.7	−1.6	4.0	62,148.7	2,120.90	2,120.79	1.15
263–E	do	149.959	149.959	30	29.287	180.6	61,961.4	107.7	−2.0	−.4	62,066.7	2,119.26	2,119.14	−.50

Even temperature 150°. Z_{150}=1,021 Int. joules per ° C. α_{150}=4.171 Int. joules per g ° C. Mean value of $\gamma_{150}=\gamma_m$=2,119.64 Int. joules per g.

249–A	July 30, 1929	169.989	170.010	15	30.777	354.7	63,345.9	52.7	5.0	−52.4	63,351.2	2,058.39	2,058.36	−.42
249–B	do	170.010	169.990	42	86.210	268.4	177,355.2	147.4	7.0	41.5	177,551.1	2,059.51	2,059.53	.75
249–C	do	169.990	169.998	15	30.775	237.6	63,356.2	52.7	4.4	−14.5	63,398.8	2,060.07	2,060.04	1.26
250–A	July 31, 1929	169.999	170.012	19	18.508	199.4	38,073.1	66.7	.9	−26.0	38,114.7	2,059.36	2,059.36	.58
251–A	Aug. 1, 1929	170.008	170.008	30	29.370	377.6	60,363.3	96.0	−2.1	−1.3	60,455.9	2,058.42	2,058.45	−.33
251–B	do	170.008	170.008	30	29.351	348.2	60,336.6	96.0	0	1.5	60,434.1	2,059.01	2,059.04	.26
251–C	do	170.008	170.000	30	29.342	318.9	60,296.5	96.0	−.4	17.6	60,409.7	2,058.81	2,058.84	.06
251–D	do	170.000	170.017	32	31.262	287.6	64,282.8	102.4	−.1	−37.4	64,347.7	2,058.34	2,058.34	−.44
251–E	do	170.017	170.000	30	29.328	258.3	60,242.8	96.0	3.5	38.1	60,380.4	2,058.80	2,058.85	.07
252–A	Aug. 2, 1929	170.036	170.018	30	30.465	375.8	62,563.2	105.3	−1.8	46.4	62,713.1	2,058.53	2,058.64	−.14
252–B	do	170.018	170.004	30	30.445	345.3	62,528.0	105.3	3.6	35.1	62,672.0	2,058.53	2,058.59	−.19
252–C	do	170.004	170.022	30	30.284	314.9	62,499.1	105.3	−3.1	−43.3	62,558.0	2,058.91	2,058.92	.14
252–D	do	170.022	170.008	30	30.407	284.5	62,460.2	105.3	−2.4	30.9	62,594.0	2,058.54	2,058.61	−.17
252–E	do	170.008	170.013	30	30.374	254.1	62,430.3	105.3	−.6	−10.8	62,524.2	2,058.48	2,058.51	−.27
252–F	do	170.013	170.014	30	30.372	223.8	62,403.8	105.3	2.1	−1.6	62,509.6	2,058.13	2,058.17	−.61
252–G	do	170.014	170.009	30	30.361	193.4	62,381.1	105.3	.4	9.5	62,496.3	2,058.44	2,058.48	−.30
252–H	do	170.009	170.008	33	33.382	160.0	68,596.3	115.8	3.1	1.7	68,716.9	2,058.50	2,058.53	−.25

Even temperature 170°. Z_{170}=1,055 Int. joules per ° C. α_{170}=4.171 Int. joules per g ° C. Mean value of $\gamma_{170}=\gamma_m$=2,058.78 Int. joules per g.

TABLE 8.—*Principal data from γ experiments*—Continued

$$\gamma_1=\frac{1}{\Delta M}\{Q_E+Q_P+Q_L-[Z+M_2\alpha]_1^2\}+\frac{\Delta H}{\Delta\theta}(\theta_1-\theta_m)$$

Experiment No.	Date	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Mass of vapor removed ΔM	Mass of water remaining M_2	Total electric energy Q_E	Pump energy Q_P	Heat leak Q_L	Energy correction for final temperature difference $-[Z+M_2\alpha]_1^2$	Entire energy added	Entire energy per gram γ_1	γ_θ corrected to even temperature	Residual $\gamma_\theta-\gamma_m$
		° C.	° C.	*Minutes*	*g*	*g*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*
253–A	Aug. 3, 1929	200.023	200.030	15	30.034	274.1	58,767.8	46.5	0.3	−15.1	58,799.5	1,957.76	1,957.84	−0.12
253–B	do	200.030	200.026	20	40.055	230.0	78,318.4	62.0	2.6	8.2	78,391.2	1,957.09	1,957.20	−.76
253–C	do	200.026	200.012	15	30.032	204.0	58,717.2	46.5	.9	26.6	58,791.2	1,957.62	1,957.71	−.25
254–A	Aug. 5, 1929	200.000	200.008	31	32.908	311.9	64,374.5	96.1	1.0	−20.5	64,451.1	1,958.52	1,958.52	.56
254–B	do	200.008	200.012	29	30.790	281.1	60,184.7	89.9	.9	−8.2	60,267.3	1,957.37	1,957.39	−.57
254–C	do	200.012	200.008	30	31.823	249.3	62,233.0	93.0	.3	9.3	62,335.6	1,958.82	1,958.86	.90
254–D	do	200.008	199.997	30	31.836	217.4	62,204.2	93.0	.6	21.4	62,319.2	1,957.51	1,957.53	−.43
254–E	do	199.997	200.006	30	31.796	185.6	62,179.4	93.0	−.1	−17.2	62,255.1	1,957.95	1,957.94	−.02
255–A	Aug. 7, 1929	199.991	199.978	30	31.486	349.4	61,526.4	93.0	−.6	34.2	61,653.0	1,958.11	1,958.08	.12
255–B	do	199.978	199.980	30	31.447	317.9	61,488.5	93.0	−1.3	−3.9	61,576.3	1,958.10	1,958.02	.06
255–C	do	199.980	199.979	30	31.426	286.5	61,448.6	93.0	−2.8	1.6	61,540.4	1,958.26	1,958.19	.23
255–D	do	199.979	199.981	30	31.399	255.1	61,407.7	93.0	.8	−3.5	61,498.0	1,958.60	1,958.53	.57
255–E	do	199.981	199.979	30	31.381	223.7	61,363.5	93.0	−1.0	−2.9	61,452.6	1,958.27	1,958.20	.24
255–F	do	199.979	199.984	10	10.454	213.2	20,444.5	30.4	−.4	−10.4	20,464.1	1,957.54	1,957.47	−.49
	Even temperature 200°.	Z_{200}=1,119 Int. joules per ° C.			α_{200}=4.159 Int. joules per g ° C.		Mean value of $\gamma_{200}=\gamma_m$=1,957.96 Int. joules per g.							
256–A	Aug 8, 1929	219.974	219.986	30	31.248	359.1	58,783.8	91.2	5.9	−29.7	58,851.2	1,883.36	1,883.26	−.16
256–B	do	219.986	220.001	30	31.214	327.9	58,734.7	91.2	5.9	−37.8	58,788.1	1,883.39	1,883.34	−.08
256–C	do	220.001	220.004	31	32.226	295.7	60,626.3	94.2	.5	−7.4	60,713.6	1,883.99	1,883.99	.57
256–D	do	220.004	219.995	30	31.174	264.5	58,606.6	91.2	−1.1	20.6	58,717.3	1,883.53	1,883.55	.13
256–E	do	219.995	220.000	30	31.122	233.4	58,552.7	91.2	−1.7	−12.2	58,630.0	1,883.88	1,883.86	.44
256–F	do	220.000	220.001	30	31.110	202.3	58,493.0	91.2	−.1	−.8	58,583.3	1,883.10	1,883.10	−.32
256–G	do	220.001	219.992	32	33.157	169.1	62,347.1	97.3	.5	15.7	62,460.6	1,883.78	1,883.78	.36
257–A	Aug. 9, 1929	218.207	218.208	30	30.958	315.9	58,433.7	91.2	1.6	−2.2	68,524.3	1,890.44	1,883.50	.08
257–B	do	218.208	218.213	31	31.964	283.9	60,337.6	94.2	.5	−11.5	60,420.8	1,890.28	1,883.35	−.07
257–C	do	218.213	218.204	30	30.926	253.0	58,339.1	91.2	.8	19.7	58,450.8	1,890.02	1,883.10	−.32
257–D	do	218.204	218.202	30	30.880	221.1	58,280.1	91.2	.1	5.9	58,376.4	1,890.42	1,883.46	.04
257–E	Aug. 9, 1929	218.202	218.218	30	30.836	191.3	58,229.9	91.2	.3	−21.2	58,299.2	1,890.10	1,883.14	−.28
257–F	do	218.218	218.214	15	19.694	171.7	37,211.2	58.2	.2	−11.1	37,258.5	1,891.79	1,883.25	−.17
257–G	do	220.000	220.014	15	20.127	276.8	54,844.7	45.6	1.7	−11.1	54,837.3	1,883.21	1,883.25	−.17
257–H	do	220.014	220.012	15	20.119	256.8	54,801.1	45.6	1.5	1.8	54,839.9	1,883.50	1,883.56	.14

257–C	do	218.213	218.204	30	30.926	253.0	58,339.1	91.2	.8	19.7	58,450.8	1,890.28	1,883.35	−.07
257–D	do	218.204	218.202	30	30.880	221.1	58,280.1	91.2	.1	5.0	58,376.4	1,890.02	1,883.10	−.32
257–E	Aug. 9, 1929	218.202	218.218	30	30.830	191.5	58,229.9	91.2	−.4	−9.2	58,356.8	1,889.42	1,883.40	−.02
257–F	do	218.218	218.214	19	19.684	107.7	37,172.4	91.2	−.5	−11.5	37,267.6	1,889.72	1,883.43	−.01
258–B	do	220.000	220.014	15	29.129	376.9	54,801.1	45.6	2.5	−6.1	54,837.3	1,883.21	1,883.26	−.17
258–C	do	220.011	220.015	15	29.119	286.8	54,801.1	45.6	1.7	−11.1	54,837.3	1,883.21	1,883.26	−.17
258–D	do	220.015	220.016	15	29.116	257.7	54,794.8	45.6	1.3	−1.8	54,839.9	1,883.50	1,883.56	−.14
258–E	do	220.016	220.011	16	31.067	226.6	58,442.9	48.6	2.4	10.7	58,504.6	1,883.18	1,883.24	−.18
258–F	do	220.011	220.010	15	29.119	197.5	54,786.0	45.6	1.6	2.4	54,835.6	1,883.16	1,883.20	−.22
258–G	do	220.100	220.010	15	29.104	168.4	54,786.4	45.6	2.0	.9	54,834.9	1,884.10	1,884.14	.72
259–A	Aug. 12, 1929	220.008	220.005	60	30.388	373.2	57,044.4	182.4	−2.2	7.3	57,231.9	1,883.37	1,883.40	−.02
259–B	do	220.005	219.999	60	30.429	342.7	57,037.1	182.4	1.9	14.0	57,235.4	1,880.95	1,880.97	−2.45
259–C	do	219.999	220.012	60	30.357	312.4	57,030.3	182.4	4.0	−30.8	57,185.9	1,883.78	1,883.78	.36
259–D	do	220.012	220.018	60	30.365	282.0	57,020.8	182.4	3.4	−13.3	57,193.3	1,883.53	1,883.58	.16
259–E	do	220.021	220.005	60	30.366	220.1	56,986.8	182.4	−1.6	34.7	57,202.3	1,883.76	1,883.84	.42
Even temperature 220°. Z_{220}=1,169 Int. joules per ° C. α_{220}=4.138 Int. joules per g ° C. Mean value of $\gamma_{220}=\gamma_m$=1,883.42 Int. joules per g.														
265–A	Oct. 23, 1929	250.005	250.023	30	33.462	322.6	58,818.2	96.9	−9.4	−45.8	58,859.9	1,759.01	1,759.03	.15
265–B	do	250.023	250.011	31	34.610	288.0	60,760.7	100.1	−10.8	27.6	60,877.6	1,758.96	1,759.06	.18
259–C	do	250.016	250.004	31	34.594	219.9	60,717.7	100.1	−7.8	27.7	60,837.7	1,758.62	1,758.69	−.19
266–A	Oct. 24, 1929	250.027	249.999	32	34.514	329.6	60,534.2	103.4	−12.3	74.0	60,699.3	1,758.69	1,758.81	−.07
259–B	do	250.034	250.037	30	32.227	240.4	56,592.1	96.9	−6.8	−5.8	56,676.4	1,758.66	1,758.81	−.07
Even temperature 250°. Z_{250}=1,259 Int. joules per °C. α_{250}=4.120 Int. joules per g °C. Mean value of $\gamma_{250}=\gamma_m$=1,758.88 Int. joules per g.														
269–A	Nov. 12, 1929	269.968	269.996	28	29.112	341.4	48,513.1	88.5	−1.8	−76.0	48,523.8	1,666.80	1,666.64	1.43
269–B	do	269.996	269.950	30	31.323	310.1	51,958.1	94.8	−8.0	117.9	52,162.8	1,665.32	1,665.30	.09
269–C	do	269.950	269.985	30	31.225	278.9	51,943.4	94.8	−3.0	−85.2	51,950.0	1,663.73	1,663.48	−1.73
269–D	do	269.985	269.975	30	31.221	247.7	51,925.4	94.8	−5.3	22.7	52,037.6	1,666.75	1,666.68	1.47
269–E	do	269.975	269.997	30	31.189	216.5	51,909.5	94.8	−8.0	−49.0	51,947.3	1,665.56	1,665.44	.23
270–A	Nov. 13, 1929	270.045	270.039	30	30.623	329.8	50,949.0	94.8	−8.7	−37.5	50,997.6	1,665.34	1,665.46	.25
270–B	do	270.039	270.010	30	30.567	299.1	50,922.7	94.8	−10.4	74.8	51,081.9	1,665.70	1,665.89	.68
270–C	do	270.010	270.035	30	30.639	268.5	50,908.5	94.8	−12.5	−60.7	50,930.1	1,662.26	1,662.31	−2.90
270–D	do	270.035	270.016	30	30.616	237.9	50,902.1	94.8	−14.7	41.7	51,023.9	1,666.58	1,666.75	1.54
270–E	do	269.998	270.020	30	30.619	186.8	50,894.9	94.8	−11.2	−54.2	50,934.3	1,665.49	1,663.48	−1.73
270–F	do	270.020	269.974	20	20.433	166.4	33,917.8	63.2	−9.7	92.0	34,063.3	1,667.07	1,667.17	1.96
271–A	Nov. 14, 1929	270.045	270.006	31	32.365	350.9	53,676.4	98.0	−2.2	108.4	53,880.6	1,664.78	1,665.00	−.21
271–B	do	270.006	270.012	30	31.250	319.7	51,925.1	94.8	6.9	−17.1	52,009.7	1,664.31	1,664.34	−.87
271–C	do	270.012	270.006	30	31.264	288.4	51,904.3	94.8	−10.6	15.1	52,003.6	1,663.37	1,663.43	−1.78
271–D	do	270.006	270.002	31	32.257	256.2	53,618.4	98.0	5.1	10.9	53,732.4	1,665.76	1,665.79	.58
271–E	do	270.002	269.999	30	31.188	224.9	51,868.6	94.8	−8.1	6.1	51,961.4	1,666.07	1,666.08	.87
272–A	Nov. 15, 1929	270.047	270.036	60	31.410	364.3	52,090.9	189.6	−12.0	30.5	52,299.0	1,665.04	1,665.27	.06
272–B	do	270.036	269.995	60	31.433	332.8	52,016.2	189.6	−1.2	110.6	52,315.2	1,664.34	1,664.52	−.69
272–C	do	270.039	270.012	43	22.441	279.0	37,223.4	135.9	−18.4	70.0	37,410.9	1,667.07	1,667.26	2.05
273–A	Nov. 16, 1929	270.013	270.005	23	39.359	319.4	65,401.9	72.7	−2.2	17.9	65,490.3	1,663.92	1,663.98	−1.23
273–B	do	270.005	269.999	22	37.604	281.8	62,528.8	69.5	−3.7	14.9	62,609.5	1,664.97	1,664.99	−.22
273–C	do	269.999	269.996	20	34.120	247.6	56,772.0	63.2	−2.7	8.2	56,840.7	1,665.91	1,665.91	.70
273–D	do	269.996	270.014	20	34.104	213.5	56,738.4	63.2	−1.9	−41.2	56,758.5	1,664.28	1,664.26	−.95
273–E	do	270.014	270.006	16	27.288	186.2	45,388.8	50.6	−2.7	17.1	45,453.8	1,665.71	1,665.78	.57
273–F	do	270.006	270.021	15	25.572	160.7	42,561.2	47.4	−.3	−28.6	42,579.7	1,665.09	1,665.11	−.10
Even temperature 270°. Z_{270}=1,328 Int. joules per °C. α_{270}=4.100 Int. joules per g °C. Mean value of $\gamma_{270}=\gamma_m$=1,665.21 Int. joules per g.														

3. BETA EXPERIMENTS

An example of the record of a single determination of β, equal to $L\frac{u}{u'-u}$, is given in Table 9. This is similar to the record for a gamma experiment, but differs from it in that the total time of the experiment over which the energy account is kept is longer than the time of electric heating and removal of liquid.

TABLE 9.—*Data sheet—determination of* $L\frac{u}{u'-u}$

Experiment No. 207-C, February 21, 1929, at 240° C.

Observers: N. S. O., H. F. S., E. F. F.

Time	Thermometers—Bridge readings		Thermoelements		Electric power	
	$2n$	$2r$	t. e. 1–5	Regulating[1]	I	E
	Ohms	*Ohms*	μv.	μv.	*Amperes*	*Volts*
2.28.00	49.0813		6.1			
2.28.10	49.0814		6.1			
2.28.20	49.0815		6.2			
2.28.30				(1)		
2.28.40		49.0878	6.1			
2.28.50		49.0880	6.2			
2.29.00		49.0879	6.0			
2.29.30	49.0814		7	(1)		
2.30.00		49.0877	8	(2)	0.97450	
2.30.30	49.0811		5	(0)		
2.31.00		49.0873	5	1		
2.31.30			6	(0)		
2.32.00		49.0871	6	(0)	.97450	
2.32.30	49.0807		4	(−1)		
2.33.00		49.0870	5	(0)		Off
2.33.30	49.0806		2.2			
2.33.40	49.0805		2.0			
2.33.50	49.0806		2.1			
2.34.00				(−2)		
2.34.10		49.0870	2.0			
2.34.20		49.0871	2.1			
2.34.30		49.0870	1.9			

[1] Values in parentheses calculated from indications of t. e. 1–5.

Total heat-leak factor=+3 microvolt-minutes.
Total time of experiment, 2.28.30 to 2.34.00=330 seconds.
Total time of electric heating 2.29.00 to 2.33.00=240 seconds.

Table 10 shows the calculation of β. This calculation makes use of the following formula:

$$\beta_1=\frac{1}{\Delta M}(Q_E+Q_P+Q_L-[Z+M_2\alpha]^2_1)+\frac{\Delta H}{\Delta\theta}(\theta_1-\theta_m)$$

TABLE 10.—*Computation—determination of* $L\frac{u}{u'-u}$

EXPERIMENT NO. 207-C

Temperature	Initial	Final
$(t+t')/2$ on bridge	49.08465	49.08380
Bridge correction	.00969	.00969
R_θ	49.09434	49.09349
$R_\theta - R_0$	23.48654	23.48569
$\delta = (R_\theta - R_0)/(R_{100} - R_0)$	235.0439	235.0354
$\beta = (0.01\theta - 1)\delta$	4.9774	4.9768
Reference block temperature	240.0123	240.0122
Mean t. e. 1–5 (microvolts)	6.12	2.05
Mean t. e. 1–5 (degrees)	.0203	.0068
Temperature of calorimeter	240.0010	240.0054

CALCULATION OF ENERGY

Potentiometer	Current		Voltage
Mean reading	0.97452	Mean reading	9.9162
Potentiometer correction	.00002	Potentiometer correction	.0002
Correction for standard 0.01 ohm	−.00005	Correction for volt-box factor	.0033
Correction for volt-box current	−.00030		
		Voltage=E	9.9197
Current=I	0.97419		

Time of electric heating=240 seconds.	
Total electric energy=IEt	2,319.3 joules.
Total time of experiment=330 seconds.	
Pump power=0.0748 watts.	
Pump energy	24.7 joules.
Total heat-leak factor=+3 microvolt-minutes.	
Heat-leak coefficient=0.142 joules/microvolt-minute.	
Heat leak	.4 joules.
Change in calorimeter temperature+0.0042°.	
Factor for calorimeter temperature change=2,949 joules/degree.	
Energy for calorimeter temperature change	−11.8 joules.
Total energy supplied	2,332.6 joules.
Mass withdrawn=62.722 g.	
Energy per gram	37.190 joules/g.
Mean bridge reading during experiment=48.08421.	
Mean reference block temperature during experiment=240.0169°.	
Mean t. e. 1–5 during experiment=5.78 microvolts=0.0192°.	
Mean calorimeter temperature during experiment=239.9977°.	
Heat content at initial minus heat content at mean ($H_1 - H_m$)	0.016 joules/g.
$L\frac{u}{u'-u}$ at 240.0010°	37.206 joules/g.

The principal data from the beta experiments are assembled in Table 11 and the computation of β completed for the entire series.

TABLE 11.—*Principal data from β experiments*

$$\beta_1=\frac{1}{\Delta M}\{Q_E+Q_P+Q_L-[Z+M_2\alpha]^2_1\}+\frac{\Delta H}{\Delta\theta}(\theta_1-\theta_m)$$

Experiment No.	Date	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Mass of water removed ΔM	Mass of water remaining M_2	Total electric energy Q_E	Pump energy Q_P	Heat leak Q_L	Energy correction for final temperature difference, $-[Z+M_2\alpha]^2_1$	Total energy added	Energy added per gram removed	$\theta_1-\theta_m$	Correction for temperature variation $\frac{\Delta H}{\Delta\theta}\times(\theta_1-\theta_m)$	Correction to even temperature	β corrected to even temperature
		° C.	° C.	Minutes	g	g	Int. joules	Int. joules	Int. joules	Int. joules	Int. joules	Int. joules per g	° C.	Int. joules per g	Int. joules per g	Int. joules per g
180–A	Dec. 28, 1928	100.000	100.007	19.000	189.123	230.5	178.6	100.3	−1.4	−13.4	264.1	1.396	−0.002	−0.008	0.000	1.388
182–A	Dec. 31, 1928	100.019	100.018	14.000	140.217	278.3	121.8	73.9	−1.5	2.1	196.3	1.400	.002	.008	−.001	1.407
204–A	Feb. 18, 1929	99.827	99.830	9.333	118.829	301.9	132.3	49.3	−1.3	−6.6	173.7	1.462	−.009	−.038	.008	1.432
	Even temperature 100°. $\frac{\Delta H}{\Delta\theta}$=4.22 Int. joules per g° C. Z_{100}=956 Int. joules per ° C. α_{100}=4.169 Int. joules per g° C. Mean value of β_{100}=1.409 Int. joules per g.															
207–A	Feb. 21, 1929	110.004	109.997	3.500	69.719	352.0	102.2	18.3	−.8	15.3	135.0	1.936	.001	.004	.000	1.941
207–B	do	110.060	110.047	3.500	77.187	274.8	102.6	18.3	−.3	27.9	148.5	1.924	.009	.038	−.004	1.958
	Even temperature 110°. $\frac{\Delta H}{\Delta\theta}$=4.23 Int. joules per g° C. Z_{110}=967 Int. joules per ° C. α_{110}=4.168 Int. joules per g° C. Mean value of β_{110}=1.950 Int. joules per g.															
199–A	Feb. 12, 1929	120.011	120.016	14.333	130.590	298.1	279.4	74.2	−2.1	−11.1	340.4	2.607	.003	.013	−.001	2.623
199–B	do	120.093	120.115	14.333	120.155	303.0	294.2	74.2	.3	−49.3	319.4	2.658	−.014	−.060	−.007	2.591
203–A	Feb. 16, 1929	120.044	120.044	9.333	77.736	346.1	154.0	48.3	−.7	.0	201.6	2.593	.012	.051	−.004	2.640
203–B	do	120.114	120.113	10.333	80.539	265.6	154.9	53.5	−.4	2.1	210.1	2.609	−.001	−.004	−.009	2.596
	Even temperature 120°. $\frac{\Delta H}{\Delta\theta}$=4.25 Int. joules per g° C. Z_{120}=979 Int. joules per ° C. α_{120}=4.168 Int. joules per g° C. Mean value of β_{120}=2.613 Int. joules per g.															
205–A	Feb. 19, 1929	129.991	130.006	9.333	57.631	363.8	195.3	47.8	−.2	−38.6	204.3	3.545	−.009	−.038	.001	3.508
205–B	do	130.067	130.059	8.667	80.403	283.4	220.5	44.4	−1.3	18.9	282.5	3.514	.004	.017	−.007	3.524
206–A	Feb. 20, 1929	130.016	130.050	3.500	75.196	341.1	215.3	17.9	−.8	25.6	258.0	3.431	.008	.034	−.002	3.463
206–B	do	130.071	130.075	3.500	64.235	281.9	215.5	17.9	.0	−9.8	223.6	3.481	−.004	−.017	−.007	3.457
	Even temperature 130°. $\frac{\Delta H}{\Delta\theta}$=4.27 Int. joules per g° C. Z_{130}=992 Int. joules per ° C. α_{130}=4.169 Int. joules per g° C.															
201–A	Feb. 14, 1929	140.011	140.009	9.333	79.570	339.3	309.4	47.3	−1.1	−4.8	350.4	4.404	−.008	−.034	−.012	4.585
202–A	Feb. 15, 1929	140.011	140.005	9.333	73.166	266.1	309.5	47.3	−1.1	−16.9	338.8	4.631	−.008	−.034	−.012	4.585

201–A	Feb. 14, 1929	140.009	140.009	9.333	79.570	339.3	309.4	47.3	−1.1	4.8	360.4	4.529	−.003	−.013	−.031	4.482
202–A	Feb. 15, 1929	140.011	140.009	9.333	79.570	339.3	309.4	47.3	−1.1	4.8	360.4	4.529	−.003	−.013	−.031	4.482
202–B	do	140.097	140.105	9.333	73.166	266.1	309.5	47.3	−1.1	−16.9	338.8	4.631	−.008	−.034	−.012	4.585

Even temperature 140°. $\frac{\Delta H}{\Delta \theta}$=4.29 Int. joules per g ° C. Z_{140}=1,006 Int. joules per ° C. α_{140}=4.171 Int. joules per g ° C.

Mean value of β_{140}=4.570 Int. joules per g.

177–A	Dec. 21, 1928	150.101	150.106	10.000	152.916	261.7	824.4	95.4	.0	−10.6	909.2	5.946	.000	.000	−.015	5.931
198–A	Feb. 9, 1929	149.913	149.918	14.333	135.999	285.7	745.8	72.0	−.8	−11.1	805.9	5.926	−.003	−.013	.013	5.926
209–A	Feb. 25, 1929	149.986	149.979	5.500	56.233	365.2	285.8	27.6	−.6	16.5	329.3	5.856	−.002	−.009	.002	5.849
209–B	do	150.046	150.051	5.500	58.587	306.6	329.9	27.6	−.2	−10.6	346.7	5.918	−.002	−.009	−.007	5.902

Even temperature 150°. $\frac{\Delta H}{\Delta \theta}$=4.32 Int. joules per g ° C. Z_{150}=1,021 Int. joules per ° C. α_{150}=4.171 Int. joules per g ° C.

Mean value of β_{150}=5.902 Int. joules per g.

211–A	Feb. 27, 1929	159.936	159.938	4.500	66.586	359.7	482.2	22.4	−.4	−4.6	499.6	7.503	−.002	−.009	−.012	7.509
211–B	do	159.997	159.996	4.500	72.729	287.1	521.9	22.4	−.4	2.0	545.9	7.506	.001	.004	−.001	7.506

Even temperature 160°. $\frac{\Delta H}{\Delta \theta}$=4.35 Int. joules per g ° C. Z_{160}=1,037 Int. joules per ° C. α_{160}=4.171 Int. joules per g ° C.

Mean value of β_{160}=7.508 Int. joules per g.

203–B	Feb. 16, 1929	169.990	169.993	9.333	61.854	356.2	548.4	45.9	−.6	−7.6	586.1	9.476	−.001	−.004	.002	9.474
263–C	do	170.053	170.041	9.333	71.437	284.7	606.3	45.9	−1.1	26.9	678.0	9.491	.007	.031	−.011	9.511

Even temperature 170°. $\frac{\Delta H}{\Delta \theta}$=4.38 Int. joules per g ° C. Z_{170}=1,055 Int. joules per ° C. α_{170}=4.171 Int. joules per g ° C.

Mean value of β_{170}=9.492 Int. joules per g.

168–A	Nov. 19, 1928	200.232	200.233	24.000	128.131	296.4	2,184.0	114.5	.8	−2.3	2,297.0	17.927	−.004	−.018	−.081	17.828
171–A	Nov. 22, 1928	200.774	200.782	22.000	140.844	285.5	2,466.3	104.9	2.1	−18.4	2,554.9	18.140	−.001	−.005	−.272	17.863
173–A	Dec. 17, 1928	200.632	200.641	20.000	121.718	292.9	2,128.1	95.4	.8	−21.1	2,203.2	18.101	−.007	−.032	−.222	17.847
176–A	Dec. 20, 1928	200.215	200.230	19.000	134.847	279.4	2,355.7	90.6	4.8	−34.2	2,416.9	17.923	.000	.000	−.075	17.848
178–A	Dec. 26, 1928	200.148	200.157	20.000	132.637	288.2	2,282.3	95.4	2.6	−20.8	2,359.5	17.789	.000	.000	−.052	17.737
183–A	Jan. 2, 1929	200.172	200.180	18.625	133.674	286.4	2,313.6	88.8	−4.1	−18.4	2,379.9	17.804	.005	.023	−.060	17.767
184–A	Jan. 3, 1929	200.147	200.150	19.333	133.349	285.6	2,299.6	92.2	−1.9	−6.9	2,383.0	17.870	.003	.014	−.052	17.832
190–A	Jan. 23, 1929	200.152	200.163	19.000	139.456	277.2	2,447.7	64.8	−.1	−26.1	2,486.3	17.829	.007	.032	−.053	17.808
191–A	Jan. 24, 1929	200.250	200.255	19.333	140.607	279.0	2,436.5	92.2	.8	−11.4	2,518.1	17.909	.003	.014	−.088	17.835
196–A	Feb. 1, 1929	200.050	200.049	20.000	134.792	287.0	2,309.1	95.4	−1.3	2.3	2,405.5	17.846	.003	.014	−.018	17.842

Even temperature 200°. $\frac{\Delta H}{\Delta \theta}$=4.51 Int. joules per g ° C. Z_{200}=1,119 Int. joules per ° C. α_{200}=4.159 Int. joules per g ° C.

Mean value of β_{200}=17.821 Int. joules per g.

TABLE 11.—*Principal data from β experiments*—Continued

$$\beta_1=\frac{1}{\Delta M}\{Q_E+Q_P+Q_L-[Z+M_{2a}]^{\theta_1}\}+\frac{\Delta H}{\Delta\theta}(\theta_1-\theta_m)$$

Experiment No.	Date	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Mass of water removed ΔM	Mass of water remaining M_2	Total electric energy Q_E	Pump energy Q_P	Heat leak Q_L	Energy correction for final temperature difference, $-[Z+M_{2a}]^{\theta_1}$	Total energy added	Energy added per gram removed	$\theta_1-\theta_m$	Correction for temperature variation $\frac{\Delta H}{\Delta\theta}\times(\theta_1-\theta_m)$	Correction to even temperature	β corrected to even temperature
		° C.	° C.	*Minutes*	*g*	*g*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	*Int. joules*	° C.	*Int. joules per g*	*Int. joules per g*	*Int. joules per g*
204–B	Feb. 18, 1929	219.920	219.923	14.000	134.034	284.4	3,424.8	65.4	0.5	−7.0	3,483.7	25.991	0.001	0.005	0.038	26.034
205–C	Feb. 19, 1929	220.050	220.050	6.667	141.309	273.6	3,647.9	31.1	−.1	.7	3,679.6	26.039	.004	.018	−.024	26.033
	Even temperature 220°. $\frac{\Delta H}{\Delta\theta}$=4.62 Int. joules per g ° C. Z_{220}=1,169 Int. joules per ° C. α_{220}=4.138 Int. joules per g. ° C.															
	Mean value of β_{220}=26.034 Int. joules per g.															
206–C	Feb. 20, 1929	229.927	229.940	4.000	57.261	359.0	1,803.9	18.5	−.7	−35.9	1,785.8	31.187	−.001	−.005	.039	31.221
206–D	do	229.992	229.975	3.500	61.843	297.1	1,867.7	16.2	.1	42.2	1,926.2	31.147	.010	.047	.004	31.198
	Even temperature 230°. $\frac{\Delta H}{\Delta\theta}$=4.68 Int. joules per g ° C. Z_{230}=1,197 Int. joules per ° C. α_{230}=4.134 Int. joules per g. ° C.															
	Mean value of β_{230}=31.210 Int. joules per g.															
192–A	Jan. 25, 1929	239.986	240.007	15.333	62.817	356.8	2,323.1	70.1	1.1	−56.7	2,337.6	37.213	−.007	−.033	.009	37.189
192–B	do	240.089	240.107	14.333	68.444	288.4	2,525.0	65.5	1.9	−45.8	2,546.6	37.207	−.007	−.033	−.055	37.119
207–C	Feb. 21, 1929	240.001	240.005	5.500	62.713	354.9	2,319.3	25.1	.4	−11.8	2,333.0	37.201	.003	.014	−.001	37.214
207–D	do	240.054	240.063	5.500	65.386	289.5	2,425.4	25.1	−.2	−22.7	2,427.6	37.127	.013	.062	−.033	37.156
	Even temperature 240°. $\frac{\Delta H}{\Delta\theta}$=4.76 Int. joules per g ° C. Z_{240}=1,227 Int. joules per ° C. α_{240}=4.129 Int. joules per g. ° C.															
	Mean value of β_{240}=37.170 Int. joules per g.															
208–A	Feb. 23, 1929	249.763	249.779	5.500	65.034	355.5	2,865.8	24.9	.6	−44.1	2,847.2	43.780	−.002	−.010	.169	43.939
208–B	do	249.839	249.851	5.500	67.912	287.6	2,928.6	24.9	.9	19.3	2,973.7	43.788	.009	.044	.115	43.947
	Even temperature 250°. $\frac{\Delta H}{\Delta\theta}$=4.85 Int. joules per g ° C. Z_{250}=1,250 Int. joules per ° C. α_{250}=4.120 Int. joules per g. ° C.															
	Mean value of β_{250}=[illegible] Int. joules per g.															
175–A	Dec. 19, 1928	270.252	270.251	28.000	139.687	274.4	8,477.4	110.3	5.4	19.7	8,611.8	61.663	−.003	−.020	−.199	60.842
175–B	Dec. 21, 1928	270.200	270.192	25.000	137.092	276.2	8,235.5	110.5	5.3	19.7	8,371.0	61.061	−.004	−.020	−.595	60.927
177–B	Dec. 21, 1929	270.200	270.192	25.000	142.219	277.4	8,564.9	110.5	2.3	−22.2	8,655.5	60.860	.011	.056	−.026	60.927
177–A	Dec. 20, 1928	269.974	269.983	25.000	34.207	284.7	2,045.8	45.7	−.8	2.9	2,093.6	61.204	.003	.015	−.595	60.624

175–A																
177–B	Dec. 21, 1928	270.200	270.192	25.000	137.092	276.2	8,235.5	110.5	5.3	19.7	8,371.0	61.061	−.004	−.020	−.199	60.842
181–A	Dec. 29, 1928	269.974	269.983	25.000	142.219	277.4	8,564.9	110.5	2.3	−22.2	8,655.5	60.860	.011	.056	.026	60.927
185–A	Jan. 4, 1929	270.598	270.597	10.333	34.207	384.7	2,045.8	45.7	−.8	2.9	2,093.6	61.204	.003	.015	−.595	60.624
187–A	Jan. 18, 1929	270.347	270.295	11.000	29.485	385.3	1,598.9	48.6	−2.2	151.4	1,796.7	60.936	.034	.173	−.345	60.764
187–B	do	270.387	270.371	9.000	22.994	362.3	1,332.4	39.8	2.2	45.1	1,419.5	61.733	.021	.108	−.385	61.456
188–A	Jan. 19, 1929	270.353	270.351	8.000	32.901	329.4	1,984.2	35.4	1.2	5.4	2,026.2	61.585	.003	.015	−.351	61.249
188–B	do	270.441	270.453	8.000	31.475	298.0	1,936.3	35.4	3.1	−30.6	1,944.2	61.770	.003	.015	−.439	61.346
189–A	Jan. 22, 1929	270.077	270.075	25.000	135.841	284.5	8,196.7	79.0	10.3	−5.0	8,281.0	60.961	.005	.025	−.077	60.909
195–A	Jan. 31, 1929	270.009	270.016	25.333	137.263	284.3	8,268.4	112.0	1.7	−17.5	8,364.6	60.938	−.002	−.010	−.009	60.919

Even temperature 270°. $\frac{\Delta H}{\Delta \theta}$=5.09 Int. joules per g ° C. Z_{270}=1,328 Int. joules per ° C. α_{270}=4.100 Int. joules per g ° C.

Mean value of β_{270}=61.003 Int. joules per g.

VII. FORMULATION

1. FORMULATION OF CALORIMETRIC DATA

In what has gone before we have the record of the experime and reduction of the data yielding the values of the three charac istic properties of the fluid, namely:

$$H - L\frac{u}{u'-u},\ L\frac{u'}{u'-u},\text{ and } L\frac{u}{u'-u}$$

denoted by the symbols α, γ, and β, respectively. As a first step the formulation of the more familiar and more useful thermal prope ties of steam for engineering purposes, the experimental results a assembled, the values smoothed by means of empirical equations, a the blank spaces filled in by interpolation or by extension, usi other experimental data where necessary. This assembly and form lation is given in Table 12. The empirical equations used are al given there. It has not yet been found possible to obtain empiri equations of a simpler form to represent the experimental resu to an accuracy warranted by the experimental precision. There a possibility that a simple formula for expressing the thermal behavi of steam may eventually be discovered. Such a formula would extremely useful, particularly so if of a form well adapted to therm dynamic calculations and if in agreement with physical facts. In t meanwhile, equations lacking this ideal simplicity of form may tolerated in the operations of obtaining numerical tabulations thermal properties which result from experiment. In the prese instance fidelity to observation has not been sacrificed to superfici simplicity.

TABLE 12.—*Assembly of observed calorimetric data and comparison with formulas*

Temperature °C.	$\alpha]_0^\theta$			β_θ			γ_θ			L_θ		
	Observed	Calculated	Observed-calculated	Observed	Calculated	Observed-calculated	Observed	Calculated	Observed-calculated	Observed	Calculated	Observed-calculated
	Int. joules/g	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*
0					[1] (0.016)			2,494.04			2,494.02	
10	41.99	42.01	−0.02		(.023)			2,472.28			2,472.26	
20	83.80	83.80	.00		(.042)			2,450.21			2,450.17	
30	125.51	125.53	−.02		(.074)			2,427.80			2,427.73	
40	167.22	167.23	−.01		(.124)			2,405.02			2,404.90	
50	208.92	208.92	.00		(.200)			2,381.84			2,381.64	
60	250.61	250.61	.00		(.312)			2,358.22			2,357.91	
70	292.30	292.29	.01		(.473)			2,334.12			2,333.65	
80	333.99	333.98	.01		(.697)			2,309.52			2,308.82	
90	375.66	375.66	.00		(1.002)			2,284.38			2,283.38	
100	417.36	417.36	.00	1.409	1.408	0.001	2,258.71	2,258.65	0.06	2,257.30	2,257.24	0.06
110	459.04	459.05	−.01	1.950	1.939	.011		2,232.29			2,230.35	
120	500.72	500.75	−.03	2.613	2.621	−.008		2,205.27			2,202.65	
130	542.39	542.46	−.07	3.488	3.484	.004	2,177.15	2,177.52	−.37	2,173.67	2,174.04	−.37
140	584.09	584.16	−.07	4.570	4.563	.007		2,149.00			2,144.44	
150	625.81	625.87	−.06	5.902	5.891	.011	2,119.64	2,119.65	−.01	2,113.75	2,113.76	−.01
160	667.51	667.57	−.06	7.508	7.510	−.002		2,089.40			2,081.89	
170	709.22	709.21	.01	9.492	9.464	.028	2,058.78	2,058.18	.60	2,049.32	2,048.72	.60
180	750.92	750.94	−.02		11.799			2,025.90			2,014.10	
190	792.58	792.60	−.02		14.569			1,992.46			1,977.89	
200	834.23	834.20	.03	17.821	17.831	−.010	1,957.96	1,957.76	.20	1,940.13	1,939.93	.20
210	875.75	875.72	.03		21.649			1,921.65			1,900.00	
220	917.16	917.17	−.01	26.034	26.090	−.056	1,883.42	1,883.98	−.56	1,857.33	1,857.89	−.56
230	958.51	958.54	−.03	31.210	31.228	−.018		1,844.56			1,813.33	
240	999.83	999.84	−.01	37.170	37.144	.026		1,802.16			1,766.02	
250	1,041.09	1,041.06	.03	43.943	43.925	.018	1,758.88	1,759.51	−.63	1,714.95	1,715.59	−.64
260	1,082.23	1,082.22	.01		51.664			1,713.26			1,661.60	
270	1,123.31	1,123.32	−.01	61.003	61.014	−.011	1,665.21	1,664.52	.69	1,604.20	1,603.51	.69

[1] Values in parentheses are calculated from previously published vapor pressure and specific volume data.

$$\alpha = 1.240777 \log_{10}\frac{\theta+7}{7} + 415.2412\left(\frac{\theta}{100}\right) + 0.6912\left(\frac{\theta}{100}\right)^2 - 0.044874\left(\frac{\theta}{100}\right)^4. \quad \text{(Range 0°–170°.)}$$

$$\alpha = 412.91945\left(\frac{\theta}{100}\right) + 3.844\left(\frac{\theta}{100}\right)^3 - 0.5238\left(\frac{\theta}{100}\right)^4 + 0.0213\left(\frac{\theta}{100}\right)^6. \quad \text{(Range 170°–270°.)}$$

$$\frac{100\beta}{\theta+273.1} = \left(\frac{\theta}{100}\right)^{\frac{1}{2}}\left[0.304065 + 0.0193\left(\frac{\theta}{100}\right) + 0.00662\left(\frac{\theta}{100}\right)\right] + 0.04830. \quad \text{(Range 100°–270°.)}$$

$$L = 0.002562(374-\theta)^2 - 5.883(374-\theta) + 249.9(374-\theta)^{1/3} - 113(374-\theta)^{1/4} \quad \text{(Range 0°–270°.)}$$

Two formulas have been used for α, one of which fits the results in the range from 0° to 170° C. and the other in the range from 1 to 270° C. The formula for β fits the results in the range from 1 to 270° C. The values of β in the range from 0° to 100° C. h been computed from previously published vapor-pressure and liqu density data.

The experimental values of L have been obtained from the obser values of γ and the smoothed or calculated values of β, using t relation. $L=\gamma-\beta$. The empirical formula for L fits the experimen results to better than 1 part in 2,300. The form of this equation h been chosen in accordance with the usually accepted belief that the critical temperature (374° C.) the heat of vaporization becom 0 and approaches this value at a negative infinite rate, and that real values exist at higher temperatures. Below 100° C. the valu given by the equation are in accord with results of other observers.

The calculated values of γ are now obtained from the calculat values of L and β, completing the formulation of the propert measured calorimetrically.

2. DERIVATION OF HEAT CONTENT AND ENTROPY FROM CALORIMETRIC DATA

It is now possible to complete the formulation of heat content an entropy, using the smoothed and extended values of the calorimetr data. The results of these derivations are given in Table 13. T values of heat content of saturated liquid water, H, given in colum 2, are obtained as the sums of the values of $\alpha\Big]_0^\theta$ and of $\beta\Big]_0^\theta$, calculate in Table 12. The values of heat content of saturated vapor H' a equal to $H+L$. The calculation of entropy of the saturated liqui has been made using each of the two formulas:

$$\Phi=\int\frac{\alpha d\Theta}{\Theta^2}+\frac{H}{\Theta}=\int\frac{d\alpha}{\Theta}+\frac{\beta}{\Theta}$$

together with the two empirical equations for α, suited to the tw ranges of temperature. Thus, a check was obtained on the accurac of the computations. These are rather laborious, owing to the com plicated form of the α equations. The values of entropy, heat con tent, α, and β are mutually consistent. The values of entropy of th saturated vapor obtained by adding L/Θ to Φ, which makes thes values consistent with the values of L.

TABLE 13.—*Thermal properties of saturated water and steam derived from calorimetric measurements*

Bureau of Standards, February, 1930

Temperature, ° C.	Heat content of liquid, H	Latent heat, L	Heat content of vapor, H'	Entropy—	
				Of liquid Φ	Of vapor Φ'
	Int. Joules/g	*Int. Joules/g*	*Int. Joules/g*	*Int. Joules/g° C.*	*Int. Joules/g° C.*
	0	2,494.02	2,494.02	0	9.132
	42.02	2,472.26	2,514.28	.1511	8,884
	83.83	2,450.17	2,534.00	.2962	8.656
	125.59	2,427.73	2,553.32	.4363	8.446
	167.34	2,404.90	2,572.24	.5719	8.253
	209.11	2,381.64	2,590.75	.7032	8.074
	250.90	2,357.91	2,608.81	.8305	7.909
	292.75	2,333.65	2,626.40	.9543	7.756
	334.66	2,308.82	2,643.48	1.0746	7.613
	376.65	2,283.38	2,660.03	1.1918	7.480
	418.75	2,257.24	2,675.99	1.3064	7.356
	460.97	2,230.35	2,691.32	1.4177	7.240
	503.36	2,202.65	2,706.01	1.5268	7.130
	545.93	2,174.04	2,719.97	1.6335	7.027
	588.71	2,144.44	2,733.15	1.7381	6.929
	631.75	2,113.76	2,745.51	1.8407	6.837
	675.06	2,081.89	2,756.95	1.9416	6.749
	718.66	2,048.72	2,767.38	2.0406	6.664
	762.72	2,014.10	2,776.82	2.1384	6.584
	807.15	1,977.89	2,785.04	2.2348	6.506
	852.02	1,939.93	2,791.95	2.3299	6.430
	897.35	1,900.00	2,797.35	2.4239	6.357
	943.24	1,857.89	2,801.13	2.5169	6.285
	989.75	1,813.33	2,803.08	2.6091	6.213
	1,036.97	1,766.02	2,802.99	2.7007	6.143
	1,084.97	1,715.59	2,800.56	2.7919	6.072
	1,133.87	1,661.60	2,795.47	2.8828	6.000
	1,184.32	1,603.51	2,787.83	2.9746	5.927

3. DISCUSSION OF ACCURACY

To the user of experimental data consisting of numerical values of physical quantities, it is important to know how trustworthy the figures are. In compiling a table of the properties of steam, over a large range of conditions, from various experimental sources, the choice of the most truthful figures to take as the basis for formulation must be based on a consideration of accuracy of the experimental results.

It is not a simple problem to make an estimate of the accuracy of steam data based on calorimetric measurements, because so many factors enter, each of which contains an element of uncertainty. The experimenter is probably best acquainted with the facts which should be considered in arriving at such an appraisal. Taken together with the evidence included in a description of the work, and making due allowance for possible bias, an experimenter's own judgment as to accuracy may prove useful to the critical reader.

By careful study of all the factors which enter into the measurements, a figure can be assigned to each which represents an estimate of the magnitude of the outstanding systematic error which remains in each factor after all known corrections for standards and calibrations have been applied. Since the signs of these various outstanding sources of systematic error are unknown, they may be considered as combining fortuitously in the final result.

In addition to these, a figure can be deduced for each of the quantities measured calorimetrically, from the differences actually exhibited by individual results, which denotes an estimate of the magnitude of the error of each final result resulting from accidental errors in making the measurements.

Having made these preliminary estimates, it is possible, with the aid of the theory of probability, to combine them and finally obtain a figure which represents an estimate of the limit of variability within which it can be expected the true value lies with any certain degree of likelihood.

Such an analysis has been made of the results of the present investigation, by consideration of every source of error, both systematic and accidental, which seems to have a significant effect. The final estimate has thus been obtained for each of the three thermal properties, H, L, and H'. In each case limits have been estimated such that there is only 1 chance in 100 that the true value lies outside these limits. This is a purely arbitrary way of expressing an index of the accuracy of the results. Such an estimate admits the 1 chance in 100 of the error being greater than the index, and also admits a chance that some important source of systematic error has been overlooked or underestimated.

On this basis it is estimated that there is only 1 chance in 100 that the values given for H differ from the truth by as much as 1 part in 2,000. It is estimated to be equally unlikely that the values given for L and H' are as much as 1.5 joules per gram from the truth in the range of the experiments from 100° to 270° C.

VIII. ACKNOWLEDGMENTS

It is impossible to acknowledge adequately all the aid which has contributed to the success of this endeavor. The initiative can be attributed to George A. Orrok. His vision and forethought focused attention on the pace at which steam power development was outstripping physical knowledge of properties of steam, and his active interest enlisted the generous support of the steam industries through the American Society of Mechanical Engineers for the research project of which the present work is a part.

Manufacturers have been glad to undertake special tasks to further the work. The Hider Steel Ball Works showed an especially generous scientific interest in accepting, at a nominal cost, the problem of grinding tiny iridium-alloy balls needed in the construction of the apparatus.

Nearly every division of the Bureau of Standards has cooperated in the work, and individuals of the staff have given valuable assistance. To the skill and handicraft of William Hausstein, instrument maker, is due much of the excellence of mechanical construction of parts of the apparatus.

Without attempting to do justice individually to all who have cheerfully helped this research along, it can be said that whatever success has been attained should be credited to the hearty cooperation of many contributors.

WASHINGTON, March 26, 1930.

REVIEW OF CALORIMETRIC MEASUREMENTS ON THERMAL PROPERTIES OF SATURATED WATER AND STEAM

By Ernest F. Fiock

ABSTRACT

This review has been prepared to assemble the data which are now available the calorimetric determinations of the thermal properties of saturated water d steam and to reduce them to a uniform basis for comparison. After a careful alysis of the reports which have appeared in the literature an attempt is made point out some possible causes for the variation among the recorded results. herever it seemed desirable, a thermodynamic interpretation of the experints is given, and in a number of cases the data have been recalculated. By se means the agreement among the various determinations has been improved several instances.

It is hoped that this assembly of results presented on a uniform basis may ve as an aid to future International Steam Table Conferences in the choice of se values and tolerances for the International Skeleton Tables.

By means of deviation charts the experimental values for the heat content or thalpy of the saturated liquid and for the latent heat are exhibited and compred. The agreement is, in general, quite gratifying.

Several modern steam tables are compared graphically with one another and th the National Bureau of Standards experimental results on the thermal operties of the saturated liquid and vapor. A marked improvement in the bles is evident with the increase in scope and the reliability of the basic experiental data.

CONTENTS

	Page
I. Introduction	481
II. Notation	482
III. Analysis and reduction of source data	483
1. Determinations of heat content of the liquid	483
(*a*) Regnault	483
(*b*) Reynolds and Moorby	484
(*c*) Dieterici	485
(*d*) Barnes	488
(*e*) Callendar	491
(*f*) Jaeger and von Steinwehr	492
2. Determinations of latent heat	494
(*a*) Dieterici	494
(*b*) Griffiths	494
(*c*) A. W. Smith	495
(*d*) Richards and Mathews	497
(*e*) Henning	498
(*f*) Jakob	499
(*g*) Carlton-Sutton	499
IV. Intercomparison of experimental data	500
V. Comparison of steam tables with Bureau of Standards results	502
VI. Conclusions	505

I. INTRODUCTION

There have been numerous attempts in the past to formulate the hermal properties of water and steam, by means of equations, into ables convenient for the use of engineers. These formulations have,

through necessity, been based on scattered groups of experimen data, recorded by different investigators in a great variety of un For the most part the variations in the tabulated values in ste tables may be attributed to three causes. First, the choice of vari forms of empirical relations to fit data which in themselves are s tered and somewhat discordant; second, the confusion arising fr the use of the different measuring standards; third, the thermo namic interpretation of the experimental data.

An important advance in the evolution of steam tables was made the International Steam Table Conference at London in July, 19 One accomplishment of this conference [1] [2] [3] was the establishment an International Skeleton Table, with tolerances, of the therm properties of water and steam. It was anticipated that the ta there adopted was subject to revision by subsequent conferences wi the idea of narrowing the limits and approaching more closely t true values.

The publication of the data from the calorimetric determinatio at the Bureau of Standards, presenting new values for the therm properties of steam over a large portion of the saturation regi has suggested the need of a summary of all available data of a simil kind. This review is given as a supplement, appearing simultaneous with the detailed report of the Bureau of Standards determinations to aid in the comparison of these results with those previously pu lished. By the reduction of all the data to a uniform basis for co parison it is hoped that the review may serve as an aid in the choi of basic values and tolerances for the International Skeleton Stea Table.

It is often possible, by studying the published descriptions, to reve important evidence as to reliability, and it has been the aim in th review to bring out such evidence. It is gratifying to find that, some cases, careful analysis and reduction of published data are r warded by improvement in the agreement of the results.

The experiments in this field fall logically into two groups: (1 Determinations of the heat content or enthalpy of the liquid, and (2 determinations of the heat of vaporization. The various experiment of each group will be discussed in chronological order as far as practicable.

II. NOTATION

M = mass of fluid.
m = mass of saturated vapor.
θ = temperature, centigrade.
Θ = temperature, centigrade absolute.
π = saturation vapor pressure.
P = external pressure.
V = internal volume of container for water.
u = specific volume of saturated liquid.
u' = specific volume of saturated vapor.
x = fraction of the water which is vapor.
E_x = internal energy of entire water sample.
ϵ = internal energy per gram of saturated liquid.

[1] Eng., **128**, pp. 751–752; 1929.
[2] Zeit. des V. D. I., **73**, No. 52, pp. 1856–1858; 1929.
[3] Mech. Eng., **52**, pp. 120–122; 1930.
[4] B. S. Jour. Research, **5** (RP209), pp. 411–480; 1930.

ϵ' = internal energy per gram of saturated vapor.
H = heat content per gram of saturated liquid $(\epsilon + \pi u)$.
H' = heat content per gram of saturated vapor $(\epsilon' + \pi u')$.
L = heat of vaporization per gram $= H' - H$.

$$\alpha = H - L\frac{u}{u'-u} = H - \beta$$

$$\beta = \frac{Lu}{u'-u}$$

$$\gamma = L + L\frac{u}{u'-u} = L\frac{u'}{u'-u}$$

$$L = \Theta\frac{d\pi}{d\theta}(u'-u) \qquad \text{(Clapeyron equation)}$$

III. ANALYSIS AND REDUCTION OF SOURCE DATA

1. DETERMINATIONS OF HEAT CONTENT OF THE LIQUID

In the temperature range from 0° to 100° C. the investigations have been numerous and particularly painstaking, because the calorie was used as a primary unit of energy and much effort was expended in determining the precise relation between this and other units of energy. This latter knowledge has been necessary in order that all calorimetric data could be reduced to a common basis for comparison. As has already been attempted, a heat unit defined arbitrarily and directly in terms of mechanical units is universally adopted and used, the need for these so-called mechanical equivalents of heat vanishes so far as future work is concerned. The difficulties encountered in the preparation of this review emphasize the advantages of adopting some such arbitrarily defined heat unit.

That the experimental determination of the mechanical equivalent of heat referred to water is a difficult task is evidenced in the literature by the diversity of the results recorded. Even after the most careful attempts to reduce the experimental values to a uniform basis, there still exist divergent values for the mechanical equivalents of the various calories.

Since many of the past determinations of heat capacities and of ratios of these give little important information about the heat content, they are accorded only passing mention in this review. More important among them are determinations by Rowland,[5] Griffiths,[6] Schuster and Gannon,[7] Lüdin,[8] Callendar,[9] Romberg,[10] and Laby and Hercus.[11] The results of Barnes,[12] and of Jaeger and von Steinwehr [13] yield, on integration, values of heat content which will be discussed more fully later.

(a) REGNAULT

For a long time the classical work of Regnault [14] furnished the most reliable information available on the specific and latent heats of water.

[5] Proc. Am. Acad. of Arts & Sci., **15**, pp. 75–200; 1879.
[6] Phil. Trans. Roy. Soc. London, **A184**, pp. 361–504; 1893.
[7] Phil. Trans. Roy. Soc. London, **A186**, Pt. I, pp. 415–467; 1895.
[8] Die Abhängigkeit der specifischen Warme des Wassers von der Temperatur. Inaug. Diss., Zürich; 1895.
[9] Phil. Trans. Roy. Soc. London, **A199**, pp. 55–148; 1902.
[10] Proc. Am. Acad. of Arts & Sci., **57**, pp. 377–387; 1921–22.
[11] Phil. Trans. Roy. Soc. London, **A227**, pp. 63–92; 1927.
[12] Phil. Trans. Roy. Soc. London, **A199**, pp. 149–263; 1902.
[13] Ann. Phys., **369**, pp. 305–366; 1921.
[14] Relations des Expériences, **1**, 635–748; 1847.

At the time these researches were carried out the physical scien were in their infancy, but in spite of the many difficulties Regnau conclusions were remarkably accurate. In the 50 years that follow no similar experiments on water and steam comparable in accura are recorded.

No matter how carefully his experiments were done, they could n have yielded results as near to the truth as can now be obtained wi the aid of more advanced theory, more definitely established stan ards, and improved laboratory apparatus. It is not possible, with a considerable degree of certainty, to interpret the temperatures whi he recorded, in terms of the present international scale. For the reasons, no attempt will here be made to reduce his results to a com parative basis. They are considered instead as an important mil stone which it took years to reach, but which has now been left f behind.

(b) REYNOLDS AND MOORBY

In the experiments of Reynolds and Moorby [15] the value of the mea calorie was measured directly in terms of mechanical units with modified Froude brake. This work was done on an engineering scal and many precautions were taken to insure the precision of th results. The principal corrections were for thermal leakage and liber tion of dissolved air. Some errors were probably introduced b formation of vapor, by variations in the speed at which the drivin engine ran, and because thermometry at that time was not on a entirely satisfactory basis. On the average the water entered th brake at a temperature of about 1.3° C. and a pressure of about atmospheres and left it at a temperature of about 100° C. and a pressure of about 1.8 atmospheres. A correction was applied for th energy change due to the pressure drop through the system, so tha the value recorded is the mean specific heat of water between 1.3 and 100° C. at a constant pressure of 2 atmospheres. As the mean o 26 separate determinations Reynolds and Moorby report this mechan ical equivalent as 4.1832×10^7 ergs per gram ° C. along the 2 atmos phere line. If the figure 1.0004 [16] is taken as the ratio between the international and the absolute joule, this value becomes 4.181 international joules per gram ° C. It may be further corrected to the saturation path by the following method.

The value for the change in heat content with pressure at constant temperature can be evaluated through the relation

$$\left(\frac{\partial H}{\partial P}\right)_\theta = V - \theta\left(\frac{\partial V}{\partial \theta}\right)_p \qquad (1)$$

in which the right-hand member can be evaluated with sufficient precision from data on specific volumes and coefficients of thermal expansion given in the International Critical Tables. The corrections desired are then the products $\left(\frac{\partial H}{\partial P}\right)_\theta (1-\pi)$ when the values $\pi = 0.0066$ atmospheres at 1.3° and $\pi = 1$ atmosphere at 100° are substituted. The change in heat content along the saturation path from 1.3° to 100° is greater by $0.206 - 0.076 = 0.13$ international joules per gram than it is along the 2 atmosphere path.

[15] Phil. Trans. Roy. Soc. London, **A190,** pp. 301–422; 1897.
[16] Bureau of Standards Tech. News Bul.; April, 1930.

Reynolds and Moorby's value for the change in heat content from 1° to 100° along the saturation path becomes $4.1815 \times 98.7 + 0.13 = 412.84$ international joules per gram. The value for the change in heat content of water between 0° and 100° is obtained by adding to this the Bureau of Standards value for the change in H from 0° to 100°, $=5.49$ international joules per gram. The result thus obtained from the work of Reynolds and Moorby is 418.33 international joules per gram for the change in heat content of water between 0° and 100° along the saturation path.

(c) DIETERICI

Dieterici's [17] experiments consisted in the introduction of quartz tubes at known temperatures, first empty and then containing known masses of water, into a Bunsen ice calorimeter and observing the contraction in volume due to the fusion of ice. This contraction, which he expressed in milligrams of mercury, is a measure of the heat lost by the tube or the tube and contents when its temperature changed from the initial value θ, to 0° C. By difference the contraction due to the cooling of the water sample alone was obtained. Expressing by $Q\Big]_0^\theta$ this heat lost by the water and by C_m an integrating mean specific heat which is to be experimentally determined, Dieterici's results were evaluated through the equation

$$Q\Big]_0^\theta = m\rho\Big]_0^\theta + \Big[MC_m\theta\Big]_0^\theta \tag{2}$$

in which

$$m\rho\Big]_0^\theta = \Big[(V - Mu)\Big(\Theta\frac{d\pi}{d\theta} - \pi\Big)\Big]_0^\theta \tag{3}$$

This correction $m\rho\Big]_0^\theta$ takes into account the energy changes in the water-present vapor phase. Since the volume change of the retaining tubes due to changes in temperature and pressure is negligible, the heat exchange of the contents becomes identical with the loss of internal energy.

For any state

$$E_x = Mx\epsilon' + M(1-x)\epsilon = M\epsilon + Mx(\epsilon' - \epsilon) \tag{4}$$

and

$$V = Mxu' + M(1-x)u = Mu + Mx(u' - u) \tag{5}$$

Solving

$$x = \frac{V - Mu}{M(u' - u)} \tag{6}$$

Hence

$$E_x = M\epsilon + (V - Mu)\frac{\epsilon' - \epsilon}{u' - u} \tag{7}$$

But

$$L = \epsilon' - \epsilon + \pi(u' - u) = \Theta\frac{d\pi}{d\theta}(u' - u) \tag{8}$$

[17] Dieterici, Ann. Phys., **321**, pp. 593–620; 1905.

Hence

$$\frac{\epsilon'-\epsilon}{u'-u}=\Theta\frac{d\pi}{d\theta}-\pi$$

and

$$E_x=M\epsilon+(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right)$$

But

$$Q\Big]_0^\theta=E_x\Big]_0^\theta=\Big[MC_m\theta\Big]_0^\theta+\left[(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right)\right]_0^\theta$$

From which

$$\Big[C_m\theta\Big]_0^\theta=\epsilon\Big]_0^\theta$$

Dieterici records experimental values of C_m and θ, and, as shown, the product of these is the specific internal-energy change of the saturated liquid. His values of the correction term $m\rho\Big]_0^\theta=\left[(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right)\right]_0^\theta$ were calculated from the best values of u, π, and $\frac{d\pi}{d\theta}$ then available. In order that the values of the contractions which he observed in milligrams of mercury could be converted into more convenient units he made very careful direct determinations of the volume changes produced by the addition of measured quantities of electrical energy.

With the experimental data now available it is possible to interpret his results directly in international joules without reference to his experimentally determined electrical equivalent of the calorimetrically observed quantity. His results at 100° C. furnish in effect a direct determination of the equivalent of the mean calorie in terms of milligrams of mercury. This value in milligrams of mercury corresponds to the value of the mean calorie in international joules which is now known to a greater precision than he could have obtained with his observations on electrical equivalent. When this method is used to calculate the results of his measurements all difficulties arising from the evaluation of his electrical standards and from the changes which electrical units have since undergone are avoided.

From recent experiments it is possible to evaluate the correction term $m\rho]_o^\theta$ more exactly than before. At the same time a term of the magnitude πu can be introduced to convert the internal energy changes into changes of heat content.

As above

$$Q]_o^\theta=M\epsilon]_o^\theta+\left[(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right)\right]_0^\theta \tag{13}$$

But

$$\Theta\frac{d\pi}{d\theta}=\frac{L}{u'-u}=\frac{\beta}{u} \tag{14}$$

Hence

$$Q]_o^\theta=M\epsilon]_o^\theta+\left[(V-Mu)\left(\frac{\beta}{u}-\pi\right)\right]_0^\theta \tag{15}$$

Adding $M\pi u]_o^\theta$ to both sides

$$Q]_o^\theta + M\pi u]_o^\theta = M\epsilon]_o^\theta + M\pi u]_o^\theta + \left[(V - Mu)\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta \tag{16}$$

Whence

$$Q]_o^\theta + M\pi u]_o^\theta = MH]_o^\theta + \left[(V - Mu)\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta \tag{17}$$

Expanding and collecting

$$Q]_o^\theta = MH]_o^\theta + \left[V\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta - M\beta]_o^\theta \tag{18}$$

But

$$H]_o^\theta = [\alpha + \beta]_o^\theta \tag{19}$$

Hence

$$Q]_o^\theta = M\alpha]_o^\theta + \left[V\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta \tag{20}$$

Considering now the experiments at 100° C., if $Q]_0^\theta$ is expressed in milligrams of mercury and both terms in the right-hand member in international joules, we may write

$$KQ]_o^\theta = M\alpha]_o^\theta + \left[V\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta \tag{21}$$

from which the value of the conversion factor K can be determined. Values of α and β are obtainable from the previous paper,[18] and values of π and u, which enter only in the relatively small correction term, from the best sources now available. There are 13 experiments in the neighborhood of 100° each of which yields a value of K. The 13 values of K thus obtained yield a mean value of 0.27024 international joules per milligram of mercury, when the experiments are weighted according to Dieterici's estimate of their reliability. They are very consistent, the maximum deviation from the mean being about 1 in 720 and the average 1 in 1,380. The accuracy of the chosen mean value of K is doubtless greater than the experimental accuracy at temperatures other than 100°, because of the greater number of experiments performed at that temperature, and because of the comparative ease of maintaining and determining the steam point.

To transform equation (20) given above into a form convenient for the calculation of heat content, add $M\beta]_0^\theta$ to both sides and collect.

$$M\alpha]_o^\theta + M\beta]_o^\theta = 0.27024\ Q]_o^\theta - \left[V\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta + M\beta]_o^\theta = MH]_o^\theta \tag{22}$$

$$H]_o^\theta = \frac{0.27024\ Q]_o^\theta}{M} - \frac{V}{M}\left[\frac{\beta}{u} - \pi\right]_o^\theta + \beta]_o^\theta \tag{23}$$

At any temperature the terms in the right-hand member of this equation can be evaluated from the same sources as at 100°. Dieterici's data give the values of $Q]_o^\theta$ corrected for heat leak, the values of M corrected for buoyancy, and the measured values of V. Hence, $H]_o^\theta$ can be evaluated at each temperature for which data are given.

[18] See footnote 4, p. 482.

Making use of the Bureau of Standards data, his values of H h been reduced to even temperatures for convenience in making c parisons with others. Table 1 shows the results of Dieterici's periments as obtained by this method of calculation.

TABLE 1.—*Heat content of saturated liquid water calculated from Dieterici's ex ments*

Temperature, θ °C.	Heat content, H	Temperature, θ °C.	H cont
	Int. joules per g		*Int. per*
15	63.10	100	
20	83.82	110	
25	104.6	130	
30	125.6	156	
35	146.2	183	
46	192.2	200	
56	234.2	221	
65	271.8	240	
78	326.4	259	
88	368.2	303	

[1] This value has been made to correspond exactly with the Bureau of Standards value by the meth computation.

The accuracy of the temperature measurements, which were m with mercury in glass thermometers, calibrated at the Reichsanst was probably so good that the thermometry did not limit the over accuracy of the experiments. How nearly the water contain assumed the same temperature as that observed for the bath is l certain. Heat-leak corrections were small, and though there is lit discussion of how they were obtained, it is believed that they furnish only a minor portion of the error in the final results. At the high te peratures the values of V become more significant, and higher pre sion in the determination of these would have increased the accura of the results. As a whole the research seems to have been carri out with great care and skill and claims the admiration of the care reader.

(d) BARNES

Barnes [19] gives a very detailed account of his researches on the he capacity of water between 5° and 95°, using a flow calorimeter of t so-called "continuous electric" type designed in cooperation wi Callendar.[20]

Water was admitted into a vacuum-jacketed glass calorimeter at steady but controllable rate, and its temperature was raised by mea of an electric heater located in the stream between a pair of differenti resistance thermometers which indicated the temperature rise. T amount of water which had passed through the calorimeter w determined by weighing. The experiments were performed at constant pressure differing from the atmospheric pressure by t small pressure head used to maintain the flow.

For the electrical equivalent of the mean specific heat between 5 and 95° Barnes gives 4.1888 joules, referred to the international oh and the volt defined as 1/1.4342 of the emf of the Clark cell at 15

[19] See footnote 12, p. 483.

[20] See footnote 9, p. 483.

In a recomputation of his results in 1909 [21] he expressed the belief that the voltage of the Clark cells at 15° as used in 1902 was 1.4333. This reduces the results previously published by 1 part in 798. Thus recomputed, the value of 4.1888 joules per gram for the mean specific heat between 5° and 95° becomes 4.1835 joules per gram. Correcting for the end intervals he obtained the value 4.1849 international joules per gram for the equivalent of the mean calorie along the atmospheric-pressure path. In 1910 the value of the international volt was redesigned, using as a standard the Weston normal cell having an emf at 20° of 1.0183 international volts. In terms of this standard of 1910, Clark cells, made up according to the old specification, have an emf at 15° of 1.4328 volts.[22] This may be considered at least a probable value for the Clark cells used by Barnes in terms of the present system. This value further reduces his mechanical equivalent of the mean calorie along the atmospheric-pressure path by 1 part in 1,433, to 4.1820 international joules per gram. This value, corrected to saturation pressure, becomes 4.1830 international joules per gram.

In Laby's [23] critical discussion of the mechanical equivalent of heat, the results of Barnes, among others, are reduced to absolute units. Since the values are desired here in international units, and since Laby discusses only the 20° calorie, no comparison with the results given in his review is included.

Without reference to the report of Barnes in 1909, his values for the specific heats can be transformed into present international units as follows. In his original computations the value assigned to the Clark cell at 15° was 1.4342 volts. As stated above, the emf of Clark cells made up according to the same specifications is 1.4328 international volts. Therefore, the values of specific heat as originally reported can be transformed into present international joules by reducing them by 1 part in 512.

Barnes represents his data as finally reduced by three equations, appropriate over the temperature intervals indicated.

$$(5°\text{–}37.5°) \quad C_p = 0.99722 + 0.0000035\,(37.5-\theta)^2 + 0.00000010\,(37.5-\theta)^3 \tag{24}$$

$$(37.5°\text{–}55°) \quad C_p = 0.99722 + 0.0000035\,(\theta-37.5)^2 + 0.00000010\,(\theta-37.5)^3 \tag{25}$$

$$(50°\text{–}100°) \quad C_p = 0.99839 + 0.000120\,(\theta-55) + 0.00000025\,(\theta-55)^2 \tag{26}$$

These are in terms of his own mean calorie, and yield on integration with respect to temperature, values for the changes in heat content in mean calories. The integrated equations are

$$H]_5^{\theta} = 0.99722 - 0.00000117\,(37.5-\theta)^3 - 0.000000025\,(37.5-\theta)^4 \tag{27}$$

$$H]_{37.5}^{\theta} = 0.99722 + 0.00000117\,(\theta-37.5)^3 + 0.000000025\,(\theta-37.5)^4 \tag{28}$$

$$H]_{55}^{\theta} = 0.99839 + 0.000060\,(\theta-55)^2 + 0.000000083\,(\theta-55)^3 \tag{29}$$

To transform the values calculated from these equations into a form convenient for comparison, two further corrections are applied.

[21] Proc. Roy. Soc. London, **82**, pp. 390-395; 1909.
[22] B. S. Circular No. 60, p. 41; 1920.
[23] Proc. Phys. Soc. London, **38**, pp. 169-175; 1925-26.

Since the first equation is valid only down to 5°, the value of H^5_0 = mean calories is supplied from the Bureau of Standards data. Fur correction is necessary to reduce the results to the saturation pres for each temperature recorded. The method of calculation of th corrections has already been described. Table 2 gives the values heat content calculated from Barnes's equations, the corrections reduce them to the saturation pressures and in the last column t values along the saturation path. The figure 418.30 internatio joules per gram as derived above from Barnes's own measureme is used for the conversion of mean calories to international joules.

TABLE 2.—*Heat content from Barnes's specific heat equations*

Temperature θ	Heat content $P=1$ atmosphere, $H_{1\text{ atm.}}$	$\left(\frac{dH}{dP}\right)_\theta \times (1-\pi)$	Heat content H, $P=\pi$	Heat content H, $P=\pi$
° C.	*Mean calories/g*	*Mean calories/g*	*Mean calories/g*	*Int. joules*
10	10.03	0.02	10.05	
20	20.04	.02	20.06	
30	30.02	.02	30.04	
40	39.99	.02	40.01	
50	49.97	.02	49.99	
60	59.95	.02	59.97	
70	69.95	.01	69.96	
80	79.96	.01	79.97	
90	89.98	.00	89.98	
100	100.01	.00	100.01	

The chief uncertainty in the value of the heat content of water 100° expressed in international joules per gram from the experimen of Barnes lies in the interpretation of the emf of the Clark cells used The value which seems most probable to the reviewer is 418.2 international joules per gram.

In a glass apparatus of the type used by Barnes the evaluation of th heat leak (4 per cent of the total energy supplied in the extreme case including the heat effects observed and interpreted as due to adsorp tion or liberation of residual gas in the evacuated jacket, is a difficu task.

The temperature scale used in these experiments was substantially the same as the present international scale. Observations of tempera ture differences with the differential resistance thermometers were probably sufficiently precise. The precision with which the electrica measurements were made appears to have been ample. The assump tion that the walls of the weighing vessel always retained the same mass of liquid may have been a source of error. The possibility of formation of vapor and liberation of dissolved gas within the calorimeter are inherent in the method and the effects are difficult to evaluate.

To obtain an accuracy of better than 1 part in 1,000 in this type of experiment requires a degree of refinement in the calorimetry itself which is not easily attained. It appears that there may have been pos sible sources of systematic error, some of which have been mentioned and several of which may have exceeded 1 part in 10,000. In the absence of positive supporting evidence it seems that Barnes's esti mate of accuracy of 1 part in 10,000 may have been too optimistic.

The reader of Barnes's report is impressed with the remarkable care and skill with which the experimental program was planned and

executed, and this piece of work remains one of the outstanding contributions to our knowledge of the heat capacity of water.

(c) CALLENDAR

Callendar spent many years in the investigation and formulation of the properties of steam. In his work on the liquid he is responsible for the development of two types of calorimetry which he has described as the continuous electric method and the continuous mixture method. The former method was used by Barnes in the researches already described and the results of this investigation are correctly attributed to Callendar and Barnes. At a later date Callendar [24] alone performed experiments by the second method to test the ratios of the specific heats reported by Barnes and found good agreement between the methods. He stated that the method of mixtures was more dependable than the electric method because the heat leak was reduced from about 4 per cent to about ½ per cent of the total energy changes involved.

In not only this work of 1912 but also in all the succeeding reports which Callendar has published the reviewer has little opportunity to appraise the experimental work, as such, because practically no experimental data are given. Instead, Callendar has chosen always to formulate his experimental data through equations into tables of the properties most desired. These tables must be taken as representing the best values indicated by his own experiments, but the data of other observers are included in the reductions in such a way that it is impossible to separate them.

Beyond the knowledge that Callendar was an exceptionally brilliant, skillful, and painstaking experimenter who devoted much time to investigations in his chosen field, the lack of published experimental data precludes an estimation of the absolute accuracy of his experimental results, or the agreement between these results and his tabulated values.

Therefore, for the purposes of this comparison, the values taken from his latest steam tables [25] are used as best representative of his entire group of measurements.

Callendar's equation for the heat content of the liquid is

$$H=k(\theta-c)+\frac{Lu}{u'-u} \tag{30}$$

in which k and c are constants. The last term in this equation is the quantity β measured experimentally at the Bureau of Standards, and from the relation

$$H=\alpha+\beta \tag{31}$$

it follows directly that, according to the Callendar formula,

$$\alpha=k\ (\theta-c) \tag{32}$$

and that

$$\frac{d\alpha}{d\theta}=k \tag{33}$$

[24] Phil. Trans. Roy. Soc. London, **A212**, pp. 1–32, 1912–13.
[25] Proc. Inst. Mech. Eng., No. 3, pp. 507–527; 1929.

The quantity α has been very carefully determined by direct calorimetric measurements at this bureau at each 10° interval from 0° to 270°. These results indicate that the value of $\frac{d\alpha}{d\theta}$ is practically constant in the range 50° to 170°, but outside this range it varies considerably. Callendar recognized that his equation was inadequate in the region from 0° to the temperature of the minimum specific heat of water, but accepted it nevertheless, because of its simplicity, its degree of approximation to the truth, and the relative unimportance to the engineers of the values calculated from it in the range near the freezing point. His own experimental evidence confirming the validity of the equations at high temperatures is not at hand. According to the Bureau of Standards data the value of $\frac{d\alpha}{d\theta}$ decreases from a practically constant value of 4.17 international joules per gram °C. in the range 50° to 170° to about 4.10 international joules per gram °C. at 270°.

Since the quantity $\beta=\frac{Lu}{u'-u}$ is small in comparison with α, the discrepancy in the values of H at the higher temperatures is due largely to the difference in the evaluation of the variation of α with temperature.

Callendar's values of H' doubtless have as a basis his numerous experiments in the superheat region. His values of H are from the equation discussed above, which was based on the work of Callendar, Barnes, and probably Dieterici in the high temperature range.

In Table 3 are shown, in international joules, the values of H and H' from the most recently published Extended Steam Tables.[26]

TABLE 3.—*Callendar's values of heat content*

Temperature θ	Heat content—	
	Of liquid H	Of vapor H'
°C.	*Int. joules/g*	*Int. joules/g*
0	0	2,488.3
50	208.77	2,584.2
100	418.54	2,675.7
150	631.62	2,751.8
200	852.14	2,801.7
250	1,087.36	2,818.4
270	1,187.81	2,811.3

(f) JAEGER AND VON STEINWEHR

The experiments of Jaeger and von Steinwehr on the heat capacity of water from 5° to 50° C., performed in 1911–12 and published in 1915 [27] and more completely in 1921,[28] have been the basis for the value of the 15° calorie used by the Reichsanstalt. Their calorimeter, containing 50 liters of water at atmospheric pressure, was heated electrically, in steps of about 1.4°, and the rise in temperature was observed with resistance thermometers. A stirrer aided in the

[26] See footnote 25, p. 491.
[27] Sitzungber d. Berl. Akad., p. 424; 1915.
[28] See footnote 13, p. 483.

ribution of the heat added, and itself added mechanical energy at rate of over 60 joules per minute. The heat capacity of the rimeter, stirrer, and accessories was calculated from the masses he parts and their specific heats and was considered constant over temperature range covered. The time of electrical heating was omatically recorded with sufficient precision by a chronograph. temperature scale and the electrical units employed were sub-tially those now in use by international agreement.

The evaluation of the correction, which includes thermal leakage pump energy, was carried to considerable lengths theoretically, there is some doubt that the values so obtained were sufficiently urate. No statement was made concerning the constancy of the mp speed.

In an effort to gain sensitivity the measuring current through the rmometer was increased to 0.08 ampere. Such a procedure throws ubt upon the accurate indication of temperature changes to 0.0001°, ause of the heating of the thermometer itself. This suspicion is pported by the fact that a considerable rate of stirring was required order that the temperature change of the calorimeter would appear ular during the periods when no energy was being supplied in the ting coil. The temperature intervals were so small that the umption of the constancy of the specific heat in any interval was irely justified.

The capacity of the calorimeter was chosen so that the mass of the ter sample was large compared to the water equivalent. The calo-meter was not tightly sealed, and there was the possibility of the loss water vapor. Great care was taken with the electrical measure-nts, and the only questionable point here is the heating of the ndard 0.1 ohm resistor, due to the current in it, during observations the current through the heater.

From a total of 111 experiments 37 were rejected because of known lts in manipulation, etc. An empirical equation of specific heat a function of temperature was fitted to the remaining 74 points by e method of least squares. The consistency of the experimental ints is indicated by the fact that they lie so well on a smooth curve, e average deviation from the curve being 1 part in 2,350.

Their equation

$$C_p = 4.20477 - 0.001768\theta + 0.0000264447\theta^2 \qquad (34)$$

ields on integration with respect to temperature

$$\int_1^2 C_p d\theta = H]^2_1 = 4.20477\theta]^2_1 - 0.000884\theta^2]^2_1 + 0.0000088166\theta^3]^2_1 \qquad (35)$$

The values of changes in heat content along the atmospheric-ressure path can be computed from this equation. Corrections to he saturation path are the same as those given in the discussion of he work of Barnes.

Table 4 shows in column 2 the values of H for water under a constant ressure of 1 atmosphere from the above equation, in column 3 the orrections necessary to reduce these to saturation pressures, and in olumn 4 the values thus reduced.

TABLE 4.—*Heat content from Jaeger and von Steinwehr's specific heat equati*

Temperature θ	Heat content $P=1$ atmosphere, $H_{1\ atm.}$	$\left(\frac{\partial H}{\partial P}\right)_{\theta}(1-\pi)$	Heat content H $P=\pi$,
° C.	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*
10	41.97	0.10	42.07
20	83.82	.10	83.92
30	125.59	.09	125.68
40	167.34	.08	167.42
50	209.13	.08	209.21

2. DETERMINATIONS OF LATENT HEAT

(a) DIETERICI

Using a Bunsen ice calorimeter, Dieterici [29] made 20 determinatio of the latent heat of water at 0° C. Considering the early date this work and the comparative simplicity of his apparatus the resul seem remarkably good. He vaporized the water at pressures slight below the vapor pressure at 0° C. from small containers of glass of platinum surrounded by a considerable quantity of mercury an observed the increase in volume of the ice-water mixture in th calorimeter around the mercury. Several errors could have affecte the final results. Some water would have been lost as vapor from th capsule between the time it was weighed and the time it was co nected to the lead-in tube in the calorimeter. Some was doubtle lost as vapor to fill the tube system itself. The adiabatic expansio of the air in the system could have produced some cooling, thoug Dieterici states that this was negligible. His data for the evaluatio of the heat leaks must be taken as given because of the lack of th details of their computation. There is an uncertainty as to th amount of energy involved in the expansion of the vapor after all th liquid had evaporated. Uncertainties in units can be avoided b using the conversion factor $K=0.27024$ international joules per mill gram of mercury as derived above and based on his own determina tions of the mean calorie and the Bureau of Standards value of th electrical equivalent of the mean calorie. The 20 experiments thu reduced yield a mean value of 2,490.6 international joules per gra as the latent heat at 0° C. The average deviation of the individu experiments from this mean is 1 part in 847.

(b) GRIFFITHS

Among the earlier determinations of latent heat are those Griffiths.[30] He reported determinations by a vaporization metho under reduced pressures at 30° and 40°. That part of his apparatu in which the thermal changes were isolated and observed consiste essentially of a small oil bath, mechanically stirred and electricall heated, from which water was vaporized. This unit was located insid an iron box containing a large quantity of mercury for thermal ba last and for activating the thermoregulator which automatically main tained the temperature of the surrounding water bath. Tempera tures were observed with mercury thermometers carefully calibrate

[29] Ann. Phys., **273**, pp. 494-508; 1889.
[30] Phil. Trans. Roy. Soc. London, **A186**, Pt. I, pp. 261-342; 1895.

d corrected. Temperature differences between the calorimeter and surroundings were measured with differential platinum resistance ermometers.

Because of the method of operation adopted—namely, the evaporan of the entire water sample in the calorimeter—the end effects re rather large and troublesome. The energy supplied by the rrer amounted to about 1 per cent of the total and could be deterined to within 1 part in 50 of itself. Griffiths considered this the iting error in his experiments. The heat leak was on the average out 0.1 per cent of the total energy change involved, a fact which reases the confidence in the final results.

By passing the vapor through 18 feet of silver tube in the oil of the lorimeter proper, the danger of priming was lessened. The possiity that the vapor was superheated was small, and the likelihood error from this source is not large.

The greatest uncertainty in the reduction of these data to a comrative basis lies in the evaluation of the Clark cells used, in terms present international volts. Assuming that his cells were made up cording to the specifications of the Chicago Congress of 1893, their f on the present basis becomes 1.4328 [31] international volts. Since iffiths assigned the value 1.434 volts to his cells at 15°, his results as ven must be reduced by 1 part in 600 for conversion to present its. The individual experiments have also been corrected to even mperatures with the aid of the Bureau of Standards values of $\frac{dL}{d\theta}$.

he mean results from 7 experiments near 30° and 11 near 40° are

$L_{30°} = 2{,}426.0$ international joules per gram.
$L_{40°} = 2{,}400.5$ international joules per gram.

At 30° the individual experiments are in very good agreement, the verage deviation from the mean being 1 part in 5,170. At 40° the verage deviation from the mean is 1 part in 1,500. In spite of the reater number of experiments at 40°, it appears that the mean value 30° is probably the more accurate of the two.

(c) A. W. SMITH

A. W. Smith [32] [33] has made determinations of the heat of evapotion of water at five temperatures below 100°. He lays considerble stress on the advantages of the method which he used of allowing iet evaporation to proceed in a stream of air passing over the rface of the evaporating fluid. In the earlier work the stream of r was allowed to bubble through the water, and the stirring was ccomplished in this manner. In these experiments the corrections r thermal leakage were considered negligibly small. In the later xperiments which constituted a determination of the latent heat at 0° C., the stirring was accomplished mechanically, and the air did ot bubble through the liquid. Experiments were run at various tes and the thermal leakage and pump energy effects were thus liminated, provided they remained the same in any two experiments hich were combined. No correction was applied for the heat effect volved in the expansion of the vapor from saturation pressure down

[31] See footnote 22, p. 489.
[32] Phys. Rev., **25**, pp. 145–170; 1907.
[33] Phys. Rev., **33**, pp. 173–183; 1911.

to the partial pressure which it exerted in the mixture of air and vap
In the reports mentioned above there are not sufficient data on t
rate of passage of air to permit calculation of this correction. P
fessor Smith's privately communicated estimate is that, in the exp
ments at 100° C., the amount of air was not greater than 1 liter
5 g of water evaporated. If this maximum amount flowed in all t
experiments at 100°, the value of the latent heat from each sho
be decreased by about 1 joule per gram. For all the determinatio
below 100° where the specific volume of the vapor is relatively lar
this correction is doubtless negligibly small.

The measurements of temperature and of power supplied to t
calorimeter were sufficiently precise so that they do not limit t
accuracy of the final results.

The masses of the water evaporated were carefully determine
but where the samples were as small as 2 or 3 g, as they were in
the earlier experiments, the absolute accuracy becomes more import
and is somewhat open to question. No mention is made of the me
employed to keep the pump power constant in the stirred calorimet
A comparison of the results of the individual experiments does n
indicate a high degree or reproducibility. For instance, at 100° (
where the consistency is best, the average deviation from the mean
1 part in 1,000.

A series of four determinations at 100° was made with acti
boiling and very small flows of air. The average result of this se
is 16.7 joules per gram lower than the average of a large series in wh
the evaporation took place quietly. This low result is explained
being due to the carrying over of unevaporated droplets of water
the air-water stream.

To the reviewer it appears that the danger of priming has oft
been greatly overestimated. The experimental values for the late
heat are, in nearly every case at hand, independent of the rate
withdrawal of vapor. Mathews [34] records test experiments wh
indicate the absence of unevaporated droplets in a region above t
surface of actively boiling water.

The details of the latter series of experiments by Smith seem t
meager to justify his explanation of the low results. For the sa
reason the formulation of an alternative hypothesis is precluded.

In Table 5 are given the results of Smith's experiments. The da
recorded in the report of 1907 have been converted into present inte
national joules by decreasing the values as recorded in terms of t
Clark cell at 15° = 1.434 volts by 1 part in 600 in the latent heat
to conform to the value 1.4328 international volts as previously us
in this paper. Corrections to the temperatures indicated have be
made using the Bureau of Standards values for $\frac{dL}{d\theta}$.

TABLE 5.—*Latent heats from Smith's experiments*

Temperature	Latent heat
°C.	*Int. joules/g*
14	2,463.5
21	2,447.6
28	2,431.1
40	2,401.4
100	2,261.6

[34] J. Phys. Chem., **21**, pp. 536–569; 1917.

Application of the above-mentioned correction of 1 joule per gram r the superheating of the vapor due to its drop in pressure would duce the latent heat at 100° to 2,260.6 international joules per am. Since 1 joule per gram is the maximum to which this correc- n could have amounted, it can be stated only that according to the st information from Smith's experiments the latent heat at 100° is t less than 2,260.6 international joules per gram.

(d) RICHARDS AND MATHEWS

Determinations of latent heat at 100° by Richards and Mathews [35] d by Mathews [36] using a condensation method were carefully per- rmed. This method possesses the obvious disadvantages that curate knowledge of the heat capacity of the calorimeter and of the at content of water is necessary for the reduction of the data. lathews points out an uncertainty in the heat capacity of his calo- meter equivalent to 1 part in 500 in the latent heat, and calls ttention to the fact that the error from this source in the earlier periments was probably 2 parts in 500. Both papers assume a ean specific heat for water between 20° and 100° of 1.0012 times the ecific heat at 21.4°.

Because of so-called premature condensation it was found necessary extrapolate linearly the values of latent heat plotted against rate of ondensation to an infinite rate. Consideration of heat leak alone, hich disappears at the infinite rate, forms a more logical basis for ch a procedure. It is assumed in the following that the same ethod of operation and reduction of the data was used by Mathews that employed in the earlier work. Heat leak was measured perimentally with no flow of steam through the tube connecting the aporator and the condenser. The value so determined is greater han the true leak during an experiment because of the change in radient in the connecting tube due to the passage of hot steam rough it. On account of the warming of the lower part of the tube us produced, there is less heat flow down it from the evaporator to he calorimeter.

Let—

Q = the heat transferred to the calorimeter by the condensing steam corrected for everything except the heat leak during the flow period,

A = the heat leak per minute as determined experimentally without flow and as actually used in their reduction of the data,

B = the true heat leak per minute with steam flowing,

L_c = the latent heat as Richards and Mathews calculated it,

L = the value of latent heat as here recalculated,

M = the mass of vapor condensed, and

t = the time during which steam was flowing.

Then

$$L_c = \frac{Q - At}{M} \tag{36}$$

nd

$$L = \frac{Q - Bt}{M} \tag{37}$$

[35] J. Am. Chem. Soc., **33**, pp. 863-888: 1911.

[36] See footnote 34, p. 496.

Subtracting

$$L - L_c = \frac{(A-B)t}{M} \tag{35}$$

or

$$L = L_c + \frac{(A-B)t}{M} \tag{36}$$

As suggested above, $(A-B)$ is a positive quantity and, over the moderate range of flows used in the experiments, is probably constant. Therefore, the values of L_c as calculated by Richards and Mathews are always lower than the true experimental values by the amount $\frac{(A-B)t}{M}$. The quantity t/M is the time required for condensation of 1 g and is the abscissa of the curve used by them in the extrapolation to infinite flow. As the value of t/M increases—that is, the slower the rate of condensation—the more does L_c deviate linearly from L. It follows that the method of correction to the infinite rate was correct but that the theory of "premature condensation" was superfluous. The question of the deviations from the straight line, which might appear if the flows could be made to approach infinity, does not enter because the slope only is of importance in the calculation of the results.

The data from the 1911 paper have been recomputed, using the correction to the water equivalent which Mathews later suggested. The data from both sets of experiments have been calculated, using the Bureau of Standards values for the heat content of water.

Because two different vaporizers were employed in the earlier work the data must be treated in two parts. The results of the recalculation are given in Table 6.

TABLE 6.—*Latent heats from experiments of Richards and Mathews*

Year	Latent heat at 100°, L
	Int. joules/g
1911	2256.5
1911	2253.5
1917	2255.2

It appears that it is the systematic errors, especially the uncertainties in the heat capacities of the calorimeters, which limit the accuracy of the final results of these experiments. Professor Mathews expressed the opinion, in a private communication, that the values of the heat capacities of the calorimeters as used in these calculations are slightly low, but he did not wish to suggest definite numerical changes in them. As a heavier vaporizer was used in the second series of 1911, it may be that the water equivalent in this set should have been corrected by more than the 2 g originally suggested by Mathews.

(c) HENNING

Among the more important determinations of the latent heat of water are those of Henning.[37] [38] His method consisted essentially of

[37] Ann. Phys., **326,** pp. 849–878; 1906.

[38] Ann. Phys., **334,** pp. 441–465; 1909.

vaporizing the water from a calorimeter in a thermostatted bath and collecting the distillate in a condenser vessel in which the pressure was maintained as nearly as possible equal to the pressure in the calorimeter by means of an atmosphere of inert gas. Determinations at 11 different temperatures between 30° and 180° C. are recorded. His own reduction of these values is summarized in terms of present international units in a brief report published in 1919.[39] This summary gives values of latent heats at 10° intervals from 30° to 180°, obtained by smoothing the experimental values and interpolating with the aid of empirical equations at intermediate temperatures. His own choice of equations to best fit his data is considered adequate and probably better than one made by one less familiar with the work. Among the individual experiments at any given temperature there is rather large variation, but in general the experiments were so numerous that the effect of accidental errors on the final results has been reduced. At the higher temperatures the number of experiments was not so large, and the results are consequently less certain. In the calculation of the mass of vapor which is evaporated but remains in the calorimeter to fill the space left vacant by the removal of water, an approximation is involved, but the error from this source is negligibly small below 180°.

Table 7 shows the values which Henning recorded 1919.

TABLE 7.—*Henning's values of latent heat*

Temperature	Latent heat L	Temperature	Latent heat L
°C.	*Int. joules/g*	°C.	*Int. joules/g*
30	2, 426. 0	110	2, 228. 5
40	2, 403. 8	120	2, 200. 1
50	2, 380. 8	130	2, 170. 3
60	2, 357. 4	140	2, 139. 8
70	2, 333. 1	150	2, 109. 7
80	2, 308. 0	160	2, 079. 6
90	2, 282. 5	170	2, 049. 4
100	2, 255. 7	180	2, 019. 7

(f) JAKOB

Using a method almost identical with that of Henning, but with a new apparatus designed for use at higher temperatures, Jakob,[40] and Jakob and Fritz [41] have continued the latent-heat determinations from 180°. These reports give values through 250°, but the experiments have since been extended to about 310° C. This is an unusually comprehensive undertaking, the final results of which are not yet available. Therefore no attempt is made to include a comparison of such preliminary results of this work as are at hand with those of other experimenters.

(g) CARLTON-SUTTON

The determinations by Carlton-Sutton[42] of the latent heat at 100° deserve special prominence among the other investigations of

[39] Ann. Phys., **363,** pp. 759–760; 1919.
[40] Forschungsarbeiten V. D. I., **310**, pp. 9–19; 1928.
[41] Zeit. d. V. D. I., **73,** pp. 629–636; 1929.
[42] Proc. Roy. Soc. London, **A93,** pp. 155–176; 1916–17.

this important constant. Using a modification of Joly's classical apparatus he measured the heat of condensation of water directly in terms of the mean calorie without any reference to electrical standards. He weighed in place the steam which was condensed on a glass bulb to change its temperature from 0° to 100° C. By performing experiments, first with the bulb nearly filled with pure water and then with the bulb containing a much smaller amount of water, he was able to eliminate its heat capacity as well as many other small factors which would otherwise have appeared as corrections. The difference in the masses of steam condensed in two such experiments is that amount which would change the temperature of a mass of water corresponding to the difference of the two bulb fillings from 0° to 100°.

If the thermal conditions during the two experiments were alike, as was doubtless very nearly the case, no corrections for heat leak are required. Corrections were applied for thermal changes occuring within the bulb and for various other small elements involved in the method. The correction for the thermal changes in the bulb has been independently recomputed and found valid. Although the water in the bulb was heated under a total pressure greater than its vapor pressure, the method of calculation of the correction takes this into account and reduces the data to mean calories defined by the saturation path.

To obtain an accuracy of 1 part in 5,000 requires that the masses be accurate to 0.1 mg. In this factor the author's estimate seems somewhat optimistic. He considers that the formation of a vapor cloud upon admitting the steam into the condensing chamber at 0° is the limiting error. It seems probable that the error in determining the masses is at least as great.

The deviations among the individual determinations indicate a high degree of experimental precision.

The final reported value of 538.88 mean calories, when interpreted in terms of the Bureau of Standards mechanical equivalent of 4.1875 international joules per gram, yields for the latent heat of water at 100° the value 2,256.6 international joules per gram.

IV. INTERCOMPARISON OF EXPERIMENTAL DATA

To aid in the comparison of the data, they are assembled in tables and deviation charts. Deviations from the Bureau of Standards values as bases are plotted to facilitate the comparison of these more recent data with those published previously.

In Table 8 are shown the values of heat content of the liquid, assembled from the previous sections. By the method of computation, the result of Dieterici is made to agree exactly with that of the Bureau of Standards at 100°. Because of the uncertainty in the interpretation of the emf of the Clark cells used by Barnes, his results, expressed in international joules, involve an uncertainty of considerable magnitude. The results of Callendar are omitted in this table, but appear later in the comparisons of the steam tables. The value in the Bureau of Standards column at 303° is extrapolated and is therefore put in parentheses.

TABLE 8.—*Summary of recalculated results on heat content of the liquid*

Temperature, °C	Observer				
	Reynolds and Moorby	Barnes	Dieterici	Jaeger and von Steinwehr	Bureau of Standards
	Int. joules/g.	*Int. joules/g.*	*Int. joules/g.*	*Int. joules/g.*	*Int. joules/g.*
0		42.04		42.07	42.02
5			63.10		62.94
20		83.91	83.82	83.92	83.83
25			104.6		104.72
30		125.66	125.6	125.68	125.59
35			146.2		146.48
40		167.36		167.42	167.34
45			192.2		192.41
50		209.11		209.21	209.11
55			234.2		234.19
60		250.85			250.90
65			271.8		271.84
70		292.64			292.75
75			326.4		326.29
80		334.51			334.66
88			368.2		368.27
90		376.39			376.65
100	418.33	418.30	418.75		418.75
110			461.1		461.0
130			546.6		545.9
156			660.6		657.8
183			776.5		776.0
200			852.6		852.0
221			946.1		947.8
240			1,034.7		1,037.0
259			1,126.7		1,128.9
303			1,348.9		(1,356.3)

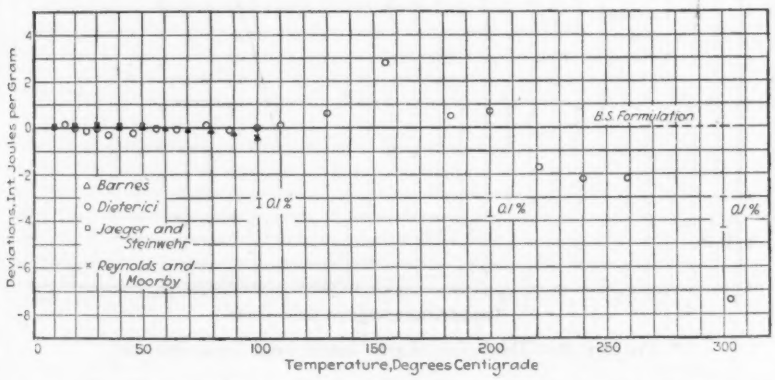


FIGURE 1.—*Deviation chart—heat content of liquid (experimental)*

Figure 1 shows the deviations of the previously published values of heat content of the liquid from the Bureau of Standards values.

In Table 9 are assembled the values of latent heat. Henning's values and those of the Bureau of Standards are calculated from empirical equations which were fitted to the data. The rest of the values are experimental points not smoothed by equations or graphically. The values in parentheses are calculated from the Bureau of Standards latent-heat equation outside the range of the experiments.

TABLE 9.—*Summary of results on latent heat*

Temperature, °C	Observer	Latent heat	Temperature, °C	Observer	Latent heat
		Int. joules/g			*Int. joules*
0	Dieterici	2, 490. 6	120	Henning	2, 200. 1
	Bureau of Standards	(2, 494. 0)		Bureau of Standards	2, 202. 7
14	Smith	2, 463. 5	130	Henning	2, 170. 3
	Bureau of Standards	(2, 463. 5)		Bureau of Standards	2, 174. 0
21	Smith	2, 447. 6	140	Henning	2, 138. 8
	Bureau of Standards	(2, 447. 9)		Bureau of Standards	2, 144. 4
28	Smith	2, 431. 1	150	Henning	2, 109. 7
	Bureau of Standards	(2, 432. 2)		Bureau of Standards	2, 113. 8
30	Griffiths	2, 426. 0	160	Henning	2, 079. 6
	Henning	2, 426. 0		Bureau of Standards	2, 081. 9
	Bureau of Standards	(2, 427. 7)	170	Henning	2, 049. 4
40	Griffiths	2, 400. 5		Bureau of Standards	2, 048. 7
	Henning	2, 403. 8	180	Henning	2, 019. 7
	Smith	2, 401. 4		Bureau of Standards	2, 014. 1
	Bureau of Standards	(2, 404. 9)	200	Bureau of Standards	1, 939. 9
50	Henning	2, 380. 8	220	Bureau of Standards	1, 857. 9
	Bureau of Standards	(2, 381. 6)	250	Bureau of Standards	1, 715. 6
60	Henning	2, 357. 4	270	Bureau of Standards	1, 603. 5
	Bureau of Standards	(2, 357. 9)			
80	Henning	2, 308. 0			
	Bureau of Standards	(2, 308. 8)			
90	Henning	2, 282. 5			
	Bureau of Standards	(2, 283. 4)			
100	Henning	2, 255. 7			
	Smith	2, 261. 6			
	Richards and Mathews	2, 256. 5			
	Richards and Mathews	2, 253. 5			
	Mathews	2, 255. 2			
	Carlton-Sutton	2, 256. 6			
	Bureau of Standards	2, 257. 2			

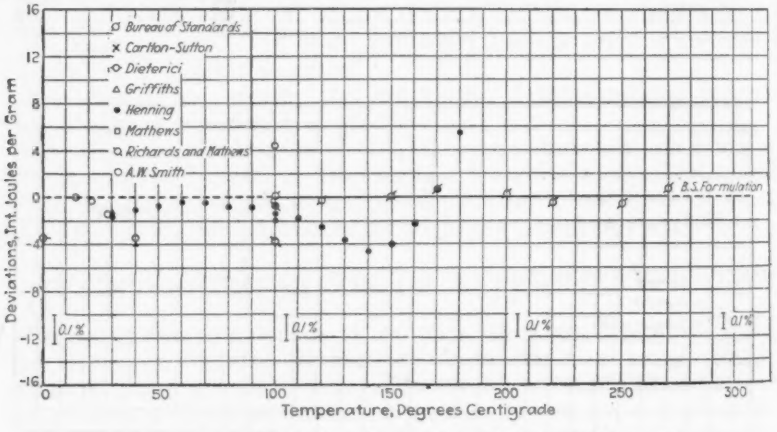


FIGURE 2.—*Deviation chart—latent heat (experimental)*

Figure 2 shows the deviations of the experimentally determined values of latent heat from the Bureau of Standards latent-heat equation.

V. COMPARISON OF STEAM TABLES WITH BUREAU OF STANDARDS RESULTS

For the purposes of this comparison, deviation charts alone are considered adequate. In Figures 3 to 6, which are largely self-explanatory, the base lines are broken in the regions not covered

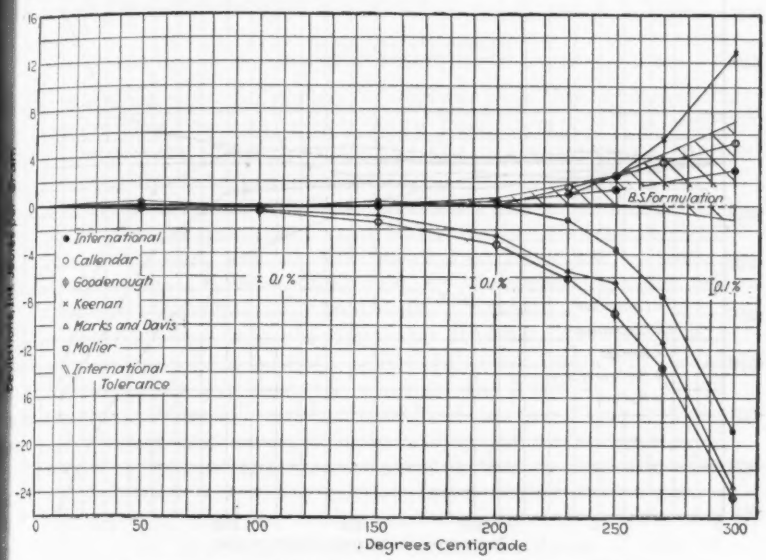


FIGURE 3.—*Deviation chart—heat content of liquid*

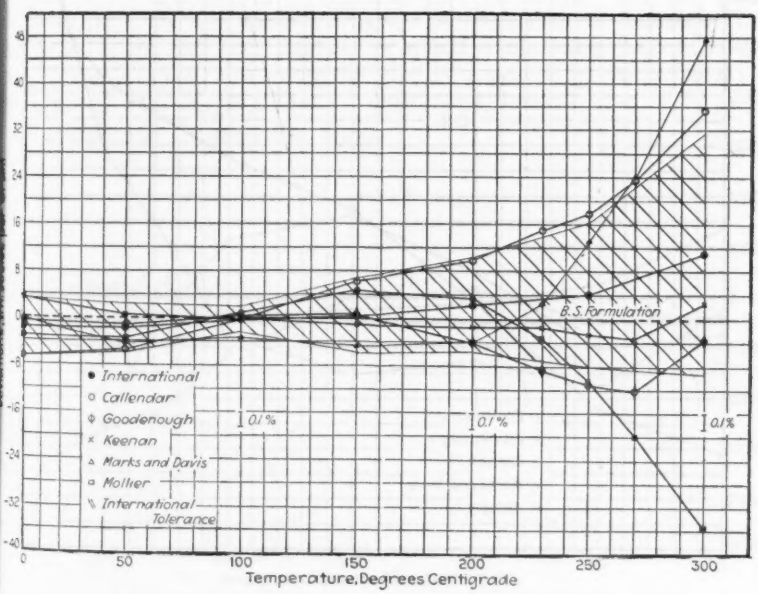


FIGURE 4.—*Deviation chart—heat content of vapor*

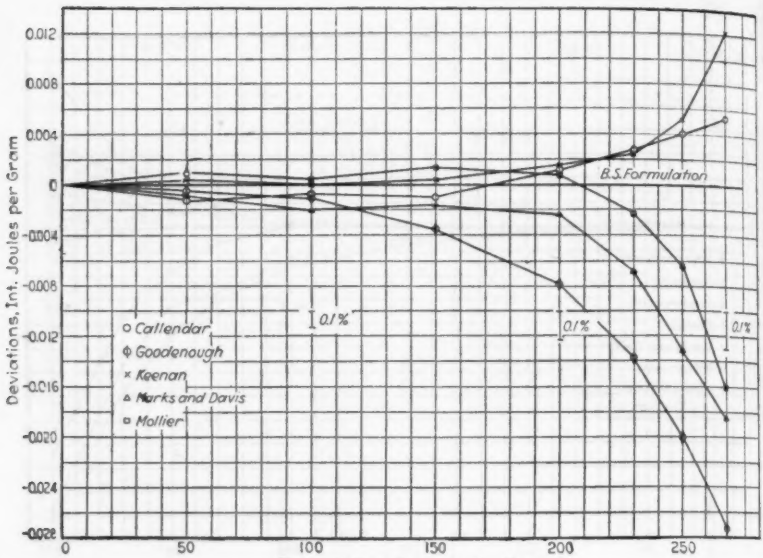


FIGURE 5.—*Deviation chart—entropy of liquid*

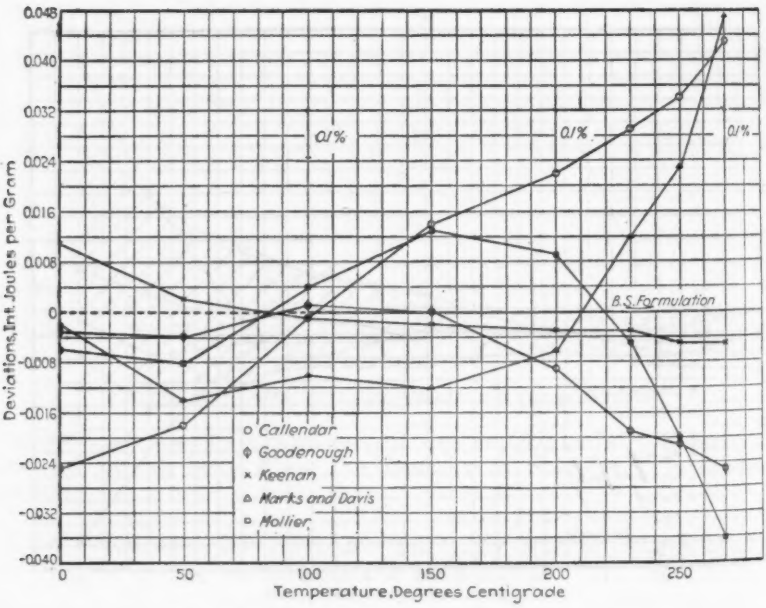


FIGURE 6.—*Deviation chart—entropy of vapor*

by the experiments. The entropy charts are included because values of entropy can be calculated directly from the Bureau of Standards calorimetric measurements.

VI. CONCLUSIONS

For the most part the reviewer believes that the agreement among the experimental results which have been compared is within the limits of the total error involved in the determinations themselves and the conversions to present units.

Referring to the heat-content determinations, the deviation of the Bureau of Standards values from those of Barnes and of Jaeger and von Steinwehr and also of the latter two from each other are, in places, somewhat greater than can be embraced by the estimates which these authors make of their own precision.

The comparisons indicate that the Bureau of Standards latent-heat equation can be used with considerable confidence in the range 0° to 100°, though it was derived solely on the basis of the experiments in the range 100° to 270° and on the classical conception of the vanishing of the latent heat at an infinite rate at the critical point.

The comparison of the steam tables indicates that the divergence in the tabulated properties of saturated water and steam is considerable. None of these tables comes completely within the limits of tolerance of the International Skeleton Steam Table of 1929, and, therefore, none can be called an International Table as specified by the London Conference. A marked improvement is evident in the tables, as more and more data of a precise nature became available for use in the formulations. It is believed that, with the progress in experimental equipment and technique and the mutual understanding of the investigators, the evolution of accurate International Tables of the thermal properties of water and steam has progressed beyond the stage of idealism and that such tables will be a reality before very many years have passed.

WASHINGTON, March 26, 1930.